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最終頁に続く

(54) 【発明の名称】 記録液およびインクジェット記録方法

(57) 【要約】

【課題】 保存安定性や吐出性に優れ、特にインクジェット記録用または筆記具用として、専用光沢紙、専用マット紙、普通紙などに記録した場合にも、印字物の印字濃度、耐擦性、耐マーカ性、耐水性、耐光性などに優れた記録液を提供する。

【解決手段】 少なくとも、顔料 (a) と、分子内にアミド結合、ウレタン結合、ウレア結合から成る群から選ばれる結合を一つ以上有し且つその遊離酸の酸価が55～350mg KOH/gである高分子 (b) とを含有し、表面張力が25～54 dyne/cmである記録液。

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## 【特許請求の範囲】

【請求項 1】 少なくとも、顔料 (a) と、分子内にアミド結合、ウレタン結合、ウレア結合から成る群から選ばれる結合を一つ以上有し且つその遊離酸の酸価が 55 ～ 350 mg KOH/g である高分子 (b) とを含有し、表面張力が 25 ～ 54 dyne/cm であることを特徴とする記録液。

【請求項 2】 高分子 (b) の遊離酸の酸価が 55 mg KOH/g 以上 150 mg KOH/g 未満である請求項 1 記載の記録液。

【請求項 3】 高分子 (b) がウレタン系樹脂である請求項 2 に記載の記録液。

【請求項 4】 高分子 (b) の遊離酸の酸価が 100 ～ 350 mg KOH/g である請求項 1 記載の記録液。

【請求項 5】 高分子 (b) がアクリルアミド誘導体および/またはメタクリルアミド誘導体を構成単位の一部とする重合体である請求項 4 に記載の記録液。

【請求項 6】 記録液の表面張力が 25 dyne/cm 以上 37 dyne/cm 未満である請求項 1 記載の記録液。

【請求項 7】 高分子 (b) がウレタン系樹脂である請求項 6 記載の記録液。

【請求項 8】 記録液の表面張力が 37 dyne/cm 以上 54 dyne/cm 未満である請求項 1 記載の記録液。

【請求項 9】 高分子 (b) がアクリルアミド誘導体および/またはメタクリルアミド誘導体を構成単位の一部とする重合体である請求項 8 記載の記録液。

【請求項 10】 高分子 (b) の遊離酸の酸価が 55 ～ 150 mg KOH/g であり、記録液の表面張力が 25 dyne/cm 以上 37 dyne/cm 未満である請求項 1 記載の記録液。

【請求項 11】 高分子 (b) がウレタン系樹脂である請求項 10 記載の記録液。

【請求項 12】 高分子 (b) の遊離酸の酸価が 100 ～ 350 mg KOH/g であり、記録液の表面張力が 37 ～ 54 dyne/cm である請求項 1 の記録液。

【請求項 13】 高分子 (b) がアクリルアミド誘導体および/またはメタクリルアミド誘導体を構成単位の一部とする重合体である請求項 12 に記載の記録液。

【請求項 14】 高分子 (b) 以外のアニオン性水溶性高分子を含有する請求項 1 に記載の記録液。

【請求項 15】 高分子 (b) 以外のアニオン性水溶性高分子の酸価が 150 mg · KOH/g 以上である請求項 14 に記載の記録液。

【請求項 16】 アニオン性水溶性高分子が (α-メチル) スチレン/(メタ) アクリル酸共重合体である請求項 14 に記載の記録液。

【請求項 17】 顔料 (a) がカーボンブラックである請求項 1 に記載の記録液。

【請求項 18】 カーボンブラックの DBP 吸油量が 100 cm<sup>3</sup>/100 g 以上である請求項 17 に記載の記録液。

【請求項 19】 非イオン系界面活性剤を 0.5 ～ 50 重量% 含む請求項 1 に記載の記録液。

【請求項 20】 支持体の少なくとも片面にインク受容層が設けられて成る記録用シートに請求項 1 に記載の記録液を使用して記録することを特徴とするインクジェット記録方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、記録液に関し、詳しくは、特にインクジェット用記録液または筆記具用記録液に適した記録液およびインクジェット記録方法に関する。

## 【0002】

【従来の技術】 従来、インクジェット記録用の記録液 (インクジェット記録液) としては、水性媒体中に酸性染料や直接染料が溶解された水性記録液 (インク) や油性染料を有機溶剤中に溶解した溶剤系記録液が使用されてきた。溶剤系記録液は、溶剤を使用するために環境安全面で問題があり、オフィスや家庭などでの使用には適さない等の理由で用途が限定されている。オフィス用や家庭用のインクジェットプリンタに使用される最も一般的な水性記録液においては、水溶性色素 (染料) を使用しているため、印字物の耐水性や耐光性が不十分であるという問題がある。そして、このようなことはインクジェット記録液のみならず、筆記具用記録液についても同様である。

【0003】 上記の問題を解決するため、水性媒体中に、色材として耐水性および耐光性に優れたカーボンブラック等の顔料を分散した記録液が一部で使用されているが、従来の記録液は、特に、印字物の耐擦性の点で不十分であり、印字物を蛍光マーカーなどで擦った場合に汚れを生じる等の問題がある。

【0004】 上記の問題を解決するため、バインダーとして種々の高分子を添加した記録液が検討されているが、粘度の上昇などの理由により吐出安定性が損なわれ、結果的に、記録液の吐出安定性、印字物の印字濃度、耐擦性および耐マーカー性の全てを満足する記録液は未だ得られていない。特に印字物の掲示などを目的とする場合は、紙や樹脂フィルム等の支持体表面にインク受容層を具備した専用記録シートに対してインクジェット方式により記録する記録方法が採用されつつある。この場合、良好な吐出性と保存安定性を得ようとする、表面の平滑ないわゆる光沢紙では印字物の耐擦性や光沢が不十分となり、表面粗度の高いいわゆるマット紙では印字物の印字濃度が不十分となる問題がある。

## 【0005】

【発明が解決しようとする課題】 本発明は、上記実情に

鑑みなされたものであり、その目的は、保存安定性や吐出性に優れ、特にインクジェット記録用または筆記具用として、専用光沢紙、専用マット紙、普通紙などに記録した場合にも、印字物の印字濃度、耐擦性、耐マーカ性、耐水性、耐光性などに優れる記録液を提供することにある。また、本発明の他の目的は、上記の記録液を使用したインクジェット記録方法を提供することにある。

#### 【0006】

【課題を解決するための手段】本発明者らは、種々検討した結果、顔料分散記録液に特定の高分子を含有させ、且つ、当該記録液の表面張力の範囲を最適化させることにより、上記の目的を容易に達成し得るとの知見を得、本発明の完成に至った。

【0007】すなわち、本発明の第1の要旨は、少なくとも、顔料(a)と、分子内にアミド結合、ウレタン結合、ウレア結合から成る群から選ばれる結合を一つ以上有し且つその遊離酸の酸価が55~350mg KOH/gである高分子(b)とを含有し、表面張力が25~54dyne/cmであることを特徴とする記録液に存する。そして、本発明の第2の要旨は、支持体の少なくとも片面にインク受容層が設けられて成る記録用シートに上記の記録液を使用して記録することを特徴とするインクジェット記録方法に存する。

#### 【0008】

【発明の実施の形態】以下、本発明を詳細に説明する。先ず、本発明で使用する顔料(a)について説明する。本発明においては、有機顔料および無機顔料の何れであってもよく、これらの具体例は次の通りである。

【0009】イエローインクに使用される顔料としては、C. I. ピグメントイエロー1、2、3、12、13、14、16、17、73、74、75、83、93、95、97、98、114、128、129、151、154等が挙げられる。マゼンタインクに使用される顔料の具体例としては、C. I. ピグメントレッド5、7、12、48(Ca)、C. I. 48(Mn)、57(Ca)、57:1、112、123、168、184、202等が挙げられる。シアンインクに使用される顔料の具体例としては、C. I. ピグメントブルー1、2、3、15:3、15:34、16、22、60、4、60等が挙げられる。

【0010】以上の他、C. I. ピグメントレッド209、122、224、177、194、C. I. ピグメントオレンジ43、C. I. バットバイオレット3、C. I. ピグメントバイオレット19、23、37、C. I. ピグメントグリーン36、7、C. I. ピグメントブルー15:6、209等も使用できる。

【0011】また、本発明においては、顔料として、アセチレンブラック、チャンネルブラック、ファーンブラック等の各種のカーボンブラックが使用できる。これらの中では、チャンネルブラック又はファーンブラック

が好ましく、特にファーンブラックが好ましい。

【0012】上記のカーボンブラックのDBP吸油量は、印字濃度の観点から、通常60ml/100g以上であるが、好ましくは100ml/100g以上、更に好ましくは140ml/100g以上である。揮発分は、通常8重量%以下、好ましくは4重量%以下である。pHは、通常1~14とされるが、記録液の保存安定性の観点から、好ましくは3~11、更に好ましくは6~9である。BET比表面積は、通常100m<sup>2</sup>/g以上とされるが、好ましくは150~600m<sup>2</sup>/g<更に好ましくは260~500m<sup>2</sup>/gである。1次粒子径は、通常30nm以下とされるが、好ましくは20nm以下、更に好ましくは16nm以下、特に好ましくは15nm以下である。ここで、DBP吸油量はJIS K6221 A法で測定した値、揮発分はJIS K6221の方法で測定した値、1次粒子径は電子顕微鏡による算術平均径(数平均)のことである。

【0013】以上の様なカーボンブラックの具体例としては、「Color BlackFW1」、「FW2」、「FW2V」、「FW18」、「FW200」、「Special Black 6」、「Color Black S170」(以上デグッサ製品)、「CONDUCTEX 975ULTRA」(コロンビアン製品)等が挙げられる。

【0014】また、本発明においては、上記の顔料を化学的に処理したもの(酸化処理、フッ素化処理など)、分散剤、界面活性剤などを物理的または化学的に結合させたもの(グラフト化処理、分散剤を分散前に予め吸着させたもの等)等を使用することが出来る。この様なものの具体例としては、Cab-o-jet 200またはCab-o-jet300(以上キャボット社製、商品名)等が挙げられる。本発明においては、上述した顔料の中では、特にカーボンブラックが好適に使用される。

【0015】次に、本発明で使用する、分子内にアミド結合、ウレタン結合、ウレア結合から成る群から選ばれる結合を一つ以上有し且つ遊離酸の酸価が55~350mg KOH/gである高分子(b)について説明する。

【0016】分子内にアミド結合を有し且つ遊離酸の酸価が55~350mg KOH/gである高分子としては、例えば、(メタ)アクリルアミド、ビニルピロリドン等のアミド結合を有する単位と(メタ)アクリル酸などの酸基を有する単位とを重合して得られる高分子の他、主鎖にアミド結合を有し且つ側鎖に酸基を有する様に合成された高分子などが挙げられる。これらの高分子は他の構成単位との共重合体として使用することが耐擦性および耐マーカ性の点で好ましい。中でも疎水性基を有する高分子が好ましい。なお、上記の(メタ)アクリルアミドとはメタクリルアミド及び/又はアクリルアミドのことを指し、(メタ)アクリル酸とはメタクリル酸及び/又はアクリル酸を指す。

【0017】上記の疎水性基としては、置換されていて  
もよいフェニル基、ベンジル基、ナフチル基などの芳香  
環を有する有機基、炭素数4以上であって且つ枝分かれ  
又は置換されていてもよいアルキル基、アルケニル基、  
アルキニル基、シクロアルキル基などが挙げられる。中  
でも、炭素数が4～10の有機基および／または芳香環  
を有する有機基が好ましい。疎水基を有する単量体の具  
体例としては、スチレン、ベンジル（メタ）アクリレー  
ト、エチルヘキシル（メタ）アクリレート、ヘキシル  
（メタ）アクリレート、ブチル（メタ）アクリレート等  
が挙げられる。

【0018】また、特に、遊離酸の酸価が100～350  
mg KOH/gである高分子（b）の具体例として  
は、アクリルアミド／エチルヘキシルメタクリレート／  
メタクリル酸共重合体、ジメチルアクリルアミド／ベン  
ジルメタクリレート／メタクリル酸共重合体、ジアセト  
ンアクリルアミド／メチルメタクリレート／ブチルアク  
リレート／メタクリル酸共重合体、メタクリルアミド／  
スチレン／アクリル酸共重合体などが挙げられる。

【0019】アミド結合を有する単量体の具体例として  
は、アクリルアミド、メタクリルアミド、ジメチルアク  
リルアミド以外にジエチルアクリルアミド、プロピルア  
クリルアミド、ジイソプロピルメタクリルアミド、ジア  
セトンアクリルアミド等のアクリルアミド誘導体および  
／またはメタクリルアミド誘導体などが使用できるが、  
アクリルアミド、メタクリルアミド、ジメチルアクリル  
アミド、ジメチルメタクリルアミド、モノメチルアクリ  
ルアミド、モノメチルメタクリルアミドが保存安定性、  
吐出安定性の点で好ましい。

【0020】高分子中におけるアミド結合を有する単量  
体の割合は、耐擦性および吐出性の観点から、通常10  
mol%以上、好ましくは10～50mol%である。  
高分子中における疎水性単量体の割合は、耐マーカ性  
の観点から、通常10mol%以上、好ましくは20mol  
%以上、更に好ましくは20mol%～70mol  
%である。高分子中におけるアミド結合を有する単量体  
の割合（mol%）と疎水性単量体の割合の比（mol  
%）は、保存安定性および吐出性の観点から、通常1/  
15以上、好ましくは1/5以上、更に好ましくは1/  
3以上である。

【0021】分子内にウレタン結合を有し且つ遊離酸の  
酸価が55～350mg KOH/gである高分子として  
は、例えば、主として、ジイソシアネート化合物と、ポ  
リエーテルジオール類、ポリエステルジオール類、ポリ  
カーボネートジオール類などのジオール化合物と、カル  
ボン酸基、スルホン酸基などの酸基含有ジオールとを反  
応して得られる水溶性ないしは水分散性の各種のウレタ  
ン系樹脂（脂肪族系ウレタン樹脂、芳香族系ウレタン樹  
脂、エステル系ウレタン樹脂、エーテル系ウレタン樹  
脂、カーボネート系ウレタン樹脂など）が挙げられる。

【0022】上記のジイソシアネートとしては、例え  
ば、ヘキサメチレンジイソシアネート、ヘキサメチレン  
ジイソシアネート、2, 2, 4-トリメチルヘキサメチ  
レンジイソシアネート等の脂肪族ジイソシアネート化合  
物、イソホロンジイソシアネート、水添キシリレンジイ  
ソシアネート、1, 4-シクロヘキサンジイソシアネー  
ト、4, 4'-ジシクロヘキシルメタンジイソシアネー  
ト等の脂環式ジイソシアネート化合物、キシリレンジイ  
ソシアネート、テトラメチルキシリレンジイソシアネート  
等の芳香脂肪族ジイソシアネート化合物、トルイレンジ  
イソシアネート、フェニルメタンジイソシアネート等の  
芳香族ジイソシアネート化合物、これらジイソシアネー  
トの変性物（カルボジイミド、ウレトジオン、ウレトイ  
ミン含有変成物など）等が挙げられる。

【0023】上記のジオール化合物とは、例えば、ポリ  
エチレングリコール、ポリプロピレングリコール、ポリ  
テトラメチレンエーテルグリコール、ポリヘキサメチ  
レンエーテルグリコール等のポリエーテルジオール、ポリ  
エチレンアジペート、ポリブチレンアジペート、ポリネ  
オペンチルアジペート、ポリ-3-メチルペンチルアジ  
ペート、ポリエチレン／ブチレンアジペート、ポリネオ  
ペンチル／ヘキシルアジペート等のポリエステルジオー  
ル、ポリカプロラクトンジオール等のポリラクトンジオ  
ール、ポリカーボネートジオールが挙げられる。特にポ  
リエーテル系またはポリエステル系のジオール化合物が  
好ましい。

【0024】上記の酸基含有ジオールとしては、例え  
ば、ジメチロール酢酸、ジメチロールプロピオン酸、ジ  
メチロール酪酸などが挙げられる。特にジメチロールプ  
ロピオン酸が好ましい。

【0025】ウレタン系樹脂はプレポリマー法によって  
合成してもよく、その際、低分子量のポリヒドロキシ化  
合物を使用してもよい。低分子量のポリヒドロキシ化合  
物としては、上記のポリエステルジオールの原料として  
挙げたグリコール及びアルキレンオキシド低モル付加  
物、グリセリン、トリメチロールエタン、トリメチロ  
ールプロパン等の3価アルコール、そのアルキレンオキシ  
ド低モル付加物などが挙げられる。

【0026】また、ウレタンプレポリマーは、ジメチロ  
ールアルカン酸に由来する酸基を中和した後または中和  
しながら水延長またはジ若しくはトリアミン延長するこ  
とが出来る。アミン延長の際に使用するポリアミンとし  
ては、通常ジアミン又はトリアミンが挙げられる。ま  
た、その具体例としてはヘキサメチレンジアミン、イソ  
ホロンジアミン、ヒドラジン、ピペラジン等が挙げられ  
る。上記の中和の際に使用する塩基としては、例えば、  
ブチルアミン、トリエチルアミン等のアルキルアミン、  
モノエタノールアミン、ジエタノールアミン、トリエタ  
ノールアミン等のアルカノールアミン、モルホリン、ア  
ンモニア、水酸化ナトリウム等の無機塩基が挙げられ

る。

【0027】分子内にウレア結合を有し且つ遊離酸の酸価が55～350mg KOH/gである高分子は、上記の水延長またはジ若しくはトリアミン延長により、ウレタン結合およびウレア結合を有する高分子として得ることが出来る。また、分子内にウレア結合のみ有する高分子の場合は、例えば、ジイソシアネートと酸基含有ジアミンとの反応によって得ることが出来る。

【0028】本発明において、高分子(b)としては、ウレタン系樹脂が好ましく、特に、エステル系、エーテル系または芳香族系のウレタン樹脂が好ましい。上記の各高分子(b)は、Li、Na、K等のアルカリ金属塩、アンモニウム、ジメチルアミン、(モノ、ジ、トリ)エタノールアミン等の有機アミン塩などの形で使用できる。

【0029】本発明で使用する上記の高分子(b)の遊離酸の酸価は、前述の通り、55～350mg KOH/gであるが、記録液の保存安定性および吐出安定性を一層高める観点から、酸価の下限は、好ましくは60mg KOH/g、更に好ましくは65mg KOH/gであり、酸価の上限は、好ましくは330mg KOH/g、更に好ましくは300mg KOH/gである。また、普通紙(および専用紙)が使用される用途(例えばデスクトップ用)に利用できる高分子(b)の遊離酸の酸価は、好ましくは100～350mg KOH/gである。更に、この場合の酸価の下限は、好ましくは120mg KOH/g、更に好ましくは150mg KOH/gであり、酸価の上限は、好ましくは330mg KOH/g、更に好ましくは300mg KOH/gである。一方、専用紙のみが使用される用途(例えばラージフォーマット用)に利用できる高分子(b)の遊離酸の酸価は好ましくは55～150mg KOH/gである。更に、この場合の酸価の下限は、好ましくは60mg KOH/g、更に好ましくは65mg KOH/gであり、酸価の上限は、好ましくは130mg KOH/g、更に好ましくは100mg KOH/gである。また、上記の高分子

(b)の重量平均分子量は、吐出安定性の観点から、通常30万以下、好ましくは5000～4万5000、更に好ましくは5000～3万、特に好ましく5000～2万である。

【0030】本発明に係る記録液には種々の添加剤を使用することが出来、例えば、各種の陰イオン性界面活性剤、ノニオン性界面活性剤、陽イオン性界面活性剤、両性界面活性剤、水溶性高分子などが挙げられる。

【0031】陰イオン性界面活性剤としては、脂肪酸塩類、アルキル硫酸エステル塩類、アルキルベンゼンスルホン酸塩類、アルキルナフタレンスルホン酸塩類、アルキルスルホコハク酸塩類、アルキルジフェニルエーテルジスルホン酸塩類、アルキルリン酸塩類、ポリオキシエチレンアルキル硫酸エステル塩類、ポリオキシエチレン

アルキルアリール硫酸エステル塩類、アルカンスルホン酸塩類、ナフタレンスルホン酸ホルマリン縮合物類、ポリオキシエチレンアルキルリン酸エステル類、N-メチル-N'-オレオイルタウリン酸塩、 $\alpha$ -オレフィンスルホン酸塩類などが挙げられる。

【0032】非イオン性界面活性剤としては、特に制限されないが、保存安定性、印字濃度の点から、エチレンオキサイド構造またはプロピレンオキサイド構造を有するものが好ましく、その中でもHLBが9～17、特に10～16のものが更に好ましい。

【0033】非イオン性界面活性剤の具体例としては、ポリオキシエチレンニルフェニルエーテル、ポリオキシエチレンオクチルフェニルエーテル、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンラウリルエーテル、ポリオキシエチレンオレイルエーテル、ポリオキシエチレントリデシルエーテル、ポリオキシエチレンセチルエーテル、ポリオキシエチレンステアリルエーテル、ポリオキシエチレンアルキルアミン、アミノポリオキシエチレン、ソルビタン脂肪酸エステル、ポリオキシエチレンソルビタンラウレート、ポリオキシエチレンソルビタンパルミテート、ポリオキシエチレンソルビタンステアレート、ポリオキシエチレンソルビタンオレエート、ナフトールエチレンオキシド付加物、アセチレングリコールエチレンオキシド付加物、ビスフェノールAエチレンオキシド付加物、オキシエチレンオキシプロピレンブロックポリマー、ソルビタン脂肪酸エステル、ポリオキシエチレンソルビタン脂肪酸エステル、ポリオキシエチレンソルビトール脂肪酸エステル、グリセリン脂肪酸エステル、ポリオキシエチレン脂肪酸エステル、ポリオキシエチレンアルキルアミン等が挙げられる。

【0034】一方、陽イオン性界面活性剤および両性界面活性剤としては、アルキルアミン塩類、第4級アンモニウム塩類、アルキルベタイン類、アミノキサイド類が挙げられる。

【0035】その他、前記の高分子(b)と共に、それ以外の各種水溶性高分子を併用してもよい。

【0036】アニオン性水溶性高分子としては、記録液の保存安定の観点から、遊離酸の形での酸価が通常150mg KOH/g以上、好ましくは200mg KOH/g以上、更に好ましく250mg KOH/g以上のものが好適である。更に、疎水性基を有する共重合体は、カーボンブラックの分散安定性、印字物の耐水性および耐擦性の点で好ましい。

【0037】高分子中の疎水性基としては、置換されていてもよいフェニル基、ベンジル基、ナフチル基などの芳香環を有する有機基、炭素数4以上であって且つ枝分かれ又は置換されていてもよいアルキル基、アルケニル基、アルキニル基、シクロアルキル基などが挙げられるが、中でも芳香環を有する有機基が好ましい。

【0038】本発明で使用するアニオン性水溶性高分子

としては、具体的には、(α-メチル) スチレン/マレイン酸共重合体、(α-メチル) スチレン/(メタ) アクリル酸共重合体、(α-メチル) スチレン/(メタ) アクリル酸エステル/(メタ) アクリル酸共重合体、

(メタ) アクリル酸エステル/(メタ) アクリル酸共重合体、(メタ) アクリル酸エステル/マレイン酸共重合体および/またはこれらの塩などが挙げられるが、好ましくは(α-メチル) スチレン/(メタ) アクリル酸共重合体である。ここで、(α-メチル) スチレンとはα-メチルスチレン及び/又はスチレンのことを指し、

(メタ) アクリル酸とはメタクリル酸および/またはアクリル酸のことを指す。

【0039】また、本発明で使用するアニオン性水溶性高分子は、ブロックポリマー、グラフトポリマー、ランダムポリマーの何れでもよいが、主に製造コストの点から、グラフトポリマー又はランダムポリマーが好ましく、特にランダムポリマーが好ましい。また、重量平均分子量は、吐出安定性の観点より、5万以下が好ましく、1万5千以下が更に好ましく、1万以下が特に好ましい。更に、酸価が150mg KOH/g以上の共重合体は、Li、Na、K等のアルカリ金属塩、アンモニア、ジメチルアミン、(モノ、ジ、トリ) エタノールアミン等の有機アミン塩などの形で使用できる。

【0040】以上の様な高分子または高分子溶液の市販品としては、ジョンソンポリマー社製の「ジョンクリル67」、「678」、「680」、「682」、「690」及び/又はその塩、「ジョンクリル52」、「57」、「60」、「62」、「63」、「70」、「354」、「501」、「6610」等が挙げられる。

【0041】本発明の記録液の媒体としては、通常、水を主体とする水性媒体が使用されるが、この場合、水に水溶性有機溶剤を添加して使用するのが好ましい。

【0042】上記の水溶性有機溶剤としては、エチレングリコール、プロピレングリコール、1、3-プロパンジオール、ブチレングリコール、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール(具体例：和光純薬社製「#200」、「#300」、「#400」、「#4000」、「#6000」)、グリセリン、N-メチルピロリドン、1、3-ジメチルイミダゾリノン、チオジグリコール、2-ピロリドン、スルホラン、ジメチルスルホキシド、ジエタノールアミン、トリエタノールアミン、メタノール、エタノール、イソプロパノール、ネオペンチルアルコール、トリメチロールプロパン、2、2-ジメチルプロパノール等が挙げられる。

【0043】本発明においては、記録液の表面張力を下げ、インクの紙面への浸透速度、記録物の乾燥速度を向上させるため、低分子量のノニオン性界面活性剤を使用することが出来る。

【0044】上記の低分子量のノニオン性界面活性剤の

具体例としては、エチレングリコールモノメチルエーテル、エチレングリコールジメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールジエチルエーテル、エチレングリコールモノ-n-プロピルエーテル、エチレングリコールモノイソプロピルエーテル、エチレングリコールモノ-n-ブチルエーテル、エチレングリコールモノ-sec-ブチルエーテル、エチレングリコールモノイソブチルエーテル、エチレングリコールモノ-tert-ブチルエーテル、エチレングリコールモノ-n-アミルエーテル、エチレングリコールモノ-n-ヘキシルエーテル、プロピレングリコールモノメチルエーテル、プロピレングリコールジメチルエーテル、プロピレングリコールモノエチルエーテル、プロピレングリコールジエチルエーテル、プロピレングリコールモノ-n-プロピルエーテル、プロピレングリコールモノイソプロピルエーテル、プロピレングリコールモノ-n-ブチルエーテル、プロピレングリコールモノ-sec-ブチルエーテル、プロピレングリコールモノイソブチルエーテル、プロピレングリコールモノ-tert-ブチルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールジメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノ-n-プロピルエーテル、ジエチレングリコールモノイソプロピルエーテル、ジエチレングリコールモノ-n-ブチルエーテル、ジエチレングリコールモノ-sec-ブチルエーテル、ジエチレングリコールモノイソブチルエーテル、ジエチレングリコールモノ-tert-ブチルエーテル、ジプロピレングリコールモノメチルエーテル、ジプロピレングリコールモノエチルエーテル、ジプロピレングリコールモノ-n-プロピルエーテル、ジプロピレングリコールモノ-n-ブチルエーテル、ポリエチレングリコールモノプロピルエーテル、ポリエチレングリコールモノブチルエーテル、グリセリンのエチレングリコール付加物(具体例：リボニックEG-1(リボケミカル社製)等)、アセチレングリコール類のエチレングリコール付加物(具体例：サーフィノール440、サーフィノール465、サーフィノール485(日信化学工業製)、アセチレノールEH、アセチレノールEL(以上、川研ファインケミカル製)等が挙げられる。

【0045】低分子量のノニオン性界面活性剤の使用量は、記録液100重量部に対し、通常0.5~50重量部、好ましくは2~30重量部、更に好ましくは5~20重量部である。記録液の表面張力は、低分子量のノニオン系界面活性剤の種類および使用量により適切に制御されるが、本発明の記録液の表面張力は25~54dyne/cmの範囲にする必要がある。表面張力が54dyne/cmより大きくなると、記録液として印字した場合に、被記録材への記録液の浸透が遅くなる結果、印刷スピードを遅くせざるを得なくなるという不具合が発

生する。また、記録液の表面張力が  $25 \text{ dyne/cm}$  より小さい範囲では被記録材への記録液の浸透が大きくなりすぎるために、印字濃度が損なわれる。

【0046】そして、上記の範囲のうち、記録液の表面張力が  $25 \text{ dyne/cm}$  以上  $37 \text{ dyne/cm}$  未満では、記録液の保存安定性、耐擦性の点で、高分子

(b) として、ウレタン系樹脂が好適に使用される。また、記録液の表面張力が  $37 \text{ dyne/cm}$  以上  $54 \text{ dyne/cm}$  未満である場合は、高分子 (b) として、  
10 アクリルアミド誘導体および／またはメタクリルアミド誘導体を構成単位の一部とする重合体が好適に使用される。

【0047】また、印刷用紙の種類から見ると、前述の普通紙（および専用紙）に使用される様な用途（例えばデスクトップ用）の場合、主に記録液の印字濃度の点で、記録液の表面張力は、通常  $37 \text{ dyne/cm}$  以上、好ましくは  $40 \text{ dyne/cm}$  以上、更に好ましくは  $40 \sim 50 \text{ dyne/cm}$  の範囲であり、また、前述の専用紙のみに使用される様な用途（例えばラージフォーマット用）の場合は、印字濃度、印字速度の点で、  
20 記録液の表面張力は、通常  $37 \text{ dyne/cm}$  未満、好ましくは  $35 \text{ dyne/cm}$  以下、更に好ましくは  $30 \sim 35 \text{ dyne/cm}$  の範囲である。

【0048】本発明の記録液には、上記の他、防腐剤、防霉剤、殺菌剤、pH調整剤、尿素などの他の添加剤を必要に応じて使用してもよい。

【0049】本発明の記録液は、公知の方法に従い、媒体中にて前記の高分子 (b) 及び必要な前記の添加成分の存在下に顔料 (a) を分散処理して高濃度の分散液を得、次いで、得られた分散液に媒体を添加して濃度調整  
30 を行つて記録液を調製する方法（マスターバッチ法）又は媒体中にて高分子 (b) 及び必要な前記の添加成分の存在下に顔料 (a) を分散処理して記録液を調製する方法によって得られる。上記のマスターバッチ法は、分散処理が高濃度で行われるために効率的である。

【0050】分散処理に使用する分散機としては、分散機としては、ボールミル、ロールミル、サンドグライン  
40 ドミルの他、メディアを使用せずに粉碎処理できるナノマイザー、アルティマイザー等のジェットミルが使用される。特に、サンドグラインドミル又はメディアに由来する汚染の少ないジェットミルが好ましい。本発明においては、上記の分散機による摩砕・分散処理の後、濾過機または遠心分離機により粗大粒子を除去する。

【0051】顔料 (a) の使用量は、記録液全重量に対し、通常  $1 \sim 10$  重量%、好ましくは  $2 \sim 8$  重量%、更に好ましくは  $2 \sim 6$  重量%である。分子内にアミド結合、ウレタン結合、ウレア結合から成る群から選ばれる結合を一つ以上有し且つ酸価が  $55 \sim 350 \text{ mg KOH/g}$  である高分子 (b) の使用量は、顔料 (a) の重量  
50 に対し、通常  $5 \sim 200$  重量%、好ましくは  $8 \sim 100$

重量%、更に好ましくは  $8 \sim 70$  重量%である。また、上記の水溶性有機溶剤の使用量は、記録液の保存安定性の観点から、記録液中の割合として、通常  $5 \sim 30$  重量%、好ましくは  $5 \sim 20$  重量%、更に好ましくは  $8 \sim 20$  重量%の範囲である。

【0052】記録液中の顔料の平均粒径は、分散安定性、吐出安定性、記録濃度の観点から、通常  $0.01 \sim 0.3 \mu\text{m}$ 、好ましくは  $0.05 \sim 0.2 \mu\text{m}$ 、更に好ましくは  $0.1 \sim 0.2 \mu\text{m}$  の範囲である。顔料の最大粒径は、分散安定性、吐出安定性の観点から、 $5 \mu\text{m}$  以下であることが好ましい。また、記録液中の顔料の分散粒径分布における標準偏差は、記録液の保存安定性、吐出安定性、記録濃度の観点から、通常  $70 \text{ nm}$  以下、好ましくは  $5 \sim 60 \text{ nm}$ 、更に好ましくは  $10 \sim 50 \text{ nm}$  とされる。

【0053】ただし、上記の平均分散粒径および分散粒径分布は、粒度分布計：日機装（株）社製品「マイクロトラック UPA150」で測定した値とする。

【0054】本発明の記録液は、インクジェット用および筆記具用に止まらず、他の用途の記録液として使用することも出来る。本発明の記録液は特にインクジェット記録用に好適である。そして、被記録材は、セルローズ、填料、サイズ剤などから成る一層構造の普通紙と、支持体の少なくとも片面にインク受容層が設けられて成る多層構造の専用紙に大別されるが、本発明の記録液は、全ての被記録材（普通紙、リサイクル紙、インクジェット専用紙（コート紙、光沢紙等）、インクジェット専用フィルム（コートフィルム、光沢フィルム等）、OHPフィルム等）に使用できる。

【0055】次に、本発明に係るインクジェット記録方法について説明する。本発明においては、オンデマンド方式、コンティニュアス方式、ピエゾ方式、サーマル方式などのあらゆるタイプのインクジェット記録方法を採用することが出来る。

【0056】本発明においては、支持体の少なくとも片面にインク受容層が設けられて成る記録用シートを使用する。

【0057】支持体としては、化学パルプ、機械パルプ、古紙パルプ等の木材パルプと顔料から成る主成分に、バインダー、サイズ剤、定着剤、歩留向上剤、カチオン化剤、紙力増強剤などの添加成分を混合し、長網抄紙機、円網抄紙機、ツインワイヤー抄紙機などの各種装置で製造した原紙が使用される。また、原紙の上にコート層を設けたアート紙、コート紙、キャストコート紙の他、ポリオレフィン等の樹脂層を設けたものも使用できる。更に、ポリエチレン、ポリプロピレン、ポリエステル、ナイロン、レーヨン、ポリウレタン、ポリエチレンテレフタレート等の合成樹脂やこれらの混合物から成るフィルム（又はシート）であってもよい。これらの支持体は、記録目的、記録画像の用途、インク受容層との密

着性などを考慮して適宜選択される。

【0058】インク受容層は、支持体の表面に無機微粒子（白色顔料）が分散されたバインダ樹脂を塗布することによって形成される。

【0059】無機微粒子としては、例えば、軽質炭酸カルシウム、重質炭酸カルシウム、カオリン、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、硫化亜鉛、炭酸亜鉛、サチンホワイト、珪酸アルミニウム、珪藻土、珪酸カルシウム、合成非晶質シリカ、水酸化アルミニウム、リトポン、ゼオライト、加水ハロイサイト、水酸化マグネシウム、アルミナゾル、ヒュームドシリカ、コロイダルシリカ等が挙げられる。また、酸化アルミニウム水和物、酸化ジルコニウム水和物、酸化スズ水和物などの金属酸化水和物から成るカチオン変性剤で被覆されたコロイダルシリカを使用することも出来る。これらの無機微粒子は、2種以上を併用してもよい。なお、無機微粒子の平均粒子径は、光沢紙とマット紙とによって異なるため、それぞれ、適切な範囲から選択される。

【0060】バインダ樹脂として、例えば、ポリビニルアルコール、酢酸ビニル、酸化澱粉、エーテル化澱粉、カルボキシメチルセルロース、ヒドロキシエチルセルロース等のセルロース誘導体、無水マレイン酸樹脂、スチレンーブタジエン共重合体、メチルメタクリレートーブタジエン共重合体などの共役ジエン系重合ラテックス類、（メタ）アクリル酸エステルの（共）重合体などのアクリル系重合ラテックス類、エチレン酢酸ビニル共重合体などのビニル系重合ラテックス類、これらの各種重合体のカルボキシル基などの官能基含有単量体による官能基変性重合ラテックス類、ポリメチルメタクリレート、ポリウレタン樹脂、塩化ビニルー酢酸ビニル共重合体、ポリビニルブチラール、カゼイン、ゼラチン、大豆蛋白、シリル変性ポリビニルアルコールの他、不飽和ポリエステル樹脂、アルキッド樹脂、メラミン樹脂、尿素樹脂などの熱硬化性合成樹脂が挙げられる。

【0061】また、本発明において、色材としてのカーボンブラックの定着性を高める目的でカチオン性有機物質を併用することが出来る。斯かるカチオン性有機物質としては、例えば、4級アンモニウム塩、アルキルアミン等のアミン類、アミド類などが挙げられる。また、この様なカチオン性残基を側鎖に有する高分子もカチオン性有機物質として使用することが出来る。

【0062】更にその他の添加剤として、顔料分散剤、増粘剤、流動性改良剤、消泡剤、抑泡剤、離型剤、発泡剤、浸透剤、着色染料、着色顔料、蛍光増白剤、酸化防止剤、防腐剤、防カビ剤、耐水化剤、湿潤紙力増強剤などを適宜配合することが出来る。

【0063】インク受容層の形成は、各種ブレードコータ、ロールコータ、エアナイフコータ、バーコータ、ロッドブレードコータ、カーテンコータ、ショートドウ

エルコータ、サイズプレス等の公知の各種装置使用して行われる。

【0064】インク受容層は多孔質層を形成しているのが好ましい。多孔質層の平均細孔径は、印字物の印字濃度および耐擦過性の観点から、通常0.5μm以上、好ましくは1μm以上、更に好ましくは2μmである。ここで、平均細孔径とは、記録シート表面の走査型電子顕微鏡写真を複数の倍率で撮影し、スキャナー入力法でデジタル化した後、コンピュータ画像解析によって抽出された各空隙部分の面積と等しい面積を有する円の直径（等面積円径）の分布を算出して求めた、算術平均径（数平均）をいう。

【0065】本発明に係る前述の記録液は、表面粗度の比較的高いマット調のインク受容層を具備した記録用シートに対して特に有用である。従って、上記のインク受容層表面のS. A. D. (Surface Area Difference) は、通常50以上、好ましくは60以上、更に好ましくは70以上とされる。この場合、極めて印字濃度および耐擦過性の優れた印字物を得ることが出来る。

【0066】上記のS. A. D. とは、表面の粗度を表す指標の一つであり、具体的には表面の比表面積を表すものであり、下記の式(1)で定義される。本発明においては、下記の表1に示す条件でS. A. D. を測定して算出する。但し、式(1)中、 $S_i$ は隣接した3つのデータポイントによって形成された全ての三角形の面積、 $P_i$ は $S_i$ をXY平面に投影した際の面積、 $\sum S_i$ は全ての $s_i$ の和、 $\sum P_i$ は全ての $P_i$ の和を表す。

【0067】

【数1】 $S. A. D. = \{ (\sum S_i / \sum P_i) - 1 \} \times 100 (\%)$

【0068】

【表1】(測定方法)

装置: Scanning Probe Microscope

機種: Digital Instruments 社製 NanoScope III

Scanner: J-Head

測定領域:  $1 \mu m \times 1 \mu m$

ピクセル数:  $512 \times 512$

Scan Rate: 1.0 Hz

測定モード: Tapping AFM

探針: デジタルインスツルメンツ社製 NCH-W

【0069】

【実施例】以下、本発明を実施例によって更に詳細に説明するが、本発明はその要旨を超えない限りこれらの実施例に限定されるものではない。以下の諸例において「部」及び「%」は、特に断りがない限り重量基準である。また、使用したカーボンブラック並びに物性の測定および評価方法は次の通りである。

【0070】

【表2】



## &lt;カーボンブラック&gt;

	窒素吸着比表面積 ( $\text{m}^2/\text{g}$ )	DBP吸油量 ( $\text{ml}/100\text{g}$ )	1次粒子径 ( $\text{nm}$ )
カーボンブラック (A)	290	150	14
カーボンブラック (B)	350	86	12

【0071】(1) 印字試験：インクジェットプリンタに記録液を充填し、インクジェットプリンタ専用紙（マ  
ット紙、光沢紙）及び／又は普通紙（コピー用紙）にベ  
タ印字して次の3段階の基準で評価した。

## 【0072】

【表3】○：印字抜けがなく且つエッジ部の品位も良好な印字物が得られた。

△：微かに印字抜けがあるが実用上問題ない。

×：印字抜けが著しい。

【0073】(2) 印字濃度評価：上記の印字試験で得た印字物の濃度をマクベス濃度計（RD914）を使用して測定した。数値が大きいほど印字濃度が良好であることを示し、1.5以上であれば合格と判定した。

【0074】(3) 耐擦性試験：上記の印字試験で得た印字物において、記録液が乾燥・定着した後に印字ベタ部を金属製スプーンで軽く擦り、次の3段階の基準で記録液の耐擦性を評価した。

## 【0075】

## 【表4】

○：記録液の剥がれがなく被記録材表面が露出しない。

△：微かに記録液の剥がれがあるが実用上問題ない。

×：記録液の剥がれが著しい。

【0076】(4) 耐マーカー試験：上記の印字試験で得た印字物において、印字試験後24時間後に文字部を黄色の市販蛍光マーカー（ZEBRA社製品OPTEX）でなぞり、次の3段階の基準でインクの耐マーカー性を評価した。

## 【0077】

【表5】○：マーカーによって擦られた文字部の汚れが殆どない。

△：マーカーによって擦られた文字部の汚れが微かにあるが、実用上問題ない。

×：マーカーによって擦られた文字部の汚れが著しい。

【0078】(5) 分散粒径分布測定：イオン交換水で記録液を希釈して粒度分布計（日機装（株）社製品「マイクロトラックUPA150」）にて分散粒径分布の測定を行った。

【0079】(6) インク受容層の平均細孔径および白色顔料の平均粒子径の測定：先ず、記録シート表面の走査型電子顕微鏡（SEM）写真（引き伸ばし後の倍率150倍）をスキャナから360dpiで入力し、コンピュータ画像処理を行いデジタル画像化した。一画素の値は0.465 $\mu\text{m}$ に対応した。512 $\times$ 512画素の6

枚の画像を同様に処理し、合計1723個の細孔（空隙部）を抽出した。抽出された各細孔の面積と等面積を有する円の直径（等面積円径）を求めて、その分布から平均細孔径（数平均値）を算出した。印字試験に供した市販のインクジェット記録専用紙についての測定結果を表9に示す。

【0080】(7) インク受容層表面のS. A. D. の測定：インク受容層表面の5点（5領域）について本文に記載の方法で測定し、その平均値を採用した。印字試験に供した市販のインクジェット記録専用紙についての測定結果を表9に示す。

【0081】(8) 表面張力測定：記録液界面張力は、ウイルヘルミー型表面張力測定機「CBVP-Z」（協和界面科学社製）を使用して測定した。

## 【0082】高分子化合物の合成例1

還流冷却器、温度計、窒素置換用ガラス管、攪拌装置を取り付けた4口フラスコにエタノール200部を入れ、AIBN（アゾビスイソブチロニトリル）2部を加え、窒素気流下80℃で還流加熱した。この反応容器に、ジメチルアクリルアミド25部、ベンジルメタクリレート44部、メタクリル酸31部、ラウリルメルカプタン5部の混合物を2時間に亘って滴下した。滴下終了後、AIBNを0.5部添加して4時間重合を行った。次いで、エタノールを除去して高分子化合物を得た。

【0083】上記の高分子化合物の酸価を測定するために、試料1gを採り、水／エタノール（50g／50g）の混合溶媒に溶解した後、0.1N KOH水溶液で中和滴定を行った。滴定はJIS K0113に記載の電位差滴定方法により行い、終点はJIS K0113 5.2.2に記載の変曲点法により決定した。滴定に必要としたKOHの量を酸価とした。その結果、上記の高分子化合物の酸価は200mg KOH/gであった。

【0084】次に、冷却下、水酸化ナトリウム水溶液をフラスコに滴下して中和した。次いで、エタノールを除去し、アニオン性高分子A水溶液を得た。この高分子は、重量平均分子量が7,000、高分子中に占めるアミド結合を有する単量体の割合が29モル%、高分子中に占める疎水基を有する単量体の割合が29モル%であった。

## 【0085】高分子の合成例2

上記の合成例1において、ジメチルアクリルアミド15部、ベンジルメタクリレート54部、メタクリル酸31部、ラウリルメルカプタン5部の混合物を使用したこと

以外は、合成例 1 と同様にして酸価が 200 mg KOH / g の高分子を得た。次いで、冷却下、水酸化ナトリウム水溶液をフラスコに滴下して中和した後、エタノールを除去し、アニオン性高分子 (B) 水溶液を得た。この高分子は、重量平均分子量が 7,500、高分子中に占めるアミド結合を有する単量体の割合が 18 モル%、高分子中に占める疎水基を有する単量体の割合が 38 モル%であった。

#### 【0086】高分子の合成例 3

上記の合成例 1 において、ジメチルアクリルアミド 45 部、ベンジルメタクリレート 24 部、メタクリル酸 31 部の混合物を使用したこと以外は、合成例 1 と同様にして酸価が 200 mg KOH / g の高分子を得た。次いで、冷却下、水酸化ナトリウム水溶液をフラスコに滴下して中和した後、エタノールを除去し、アニオン性高分子 (C) 水溶液を得た。この高分子は、重量平均分子量が 33,000、高分子中に占めるアミド結合を有する単量体の割合が 48 モル%、高分子中に占める疎水基を有する単量体の割合が 14 モル%であった。

成 分	使用量 (部)
カーボンブラック (A)	9
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル 678」(酸化: 215、Mw: 8500) のアンモニウム塩の 20 WT% 水溶液)	4.5
グリセリン	5
イオン交換水	81.5
合計	100

【0090】上記で得られた液に、後述の方法で得られたポリエステル系ウレタン樹脂溶液 (武田薬品工業株式会社製) 21.6 部、グリセリン 22.5 部、ジエチレングリコールモノブチルエーテル 22.5 部、イオン交換水 58.4 部を更に加えた。この液を No. 5C の濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は 0.139  $\mu\text{m}$  であり、記録液の表面張力は 33 dyne / cm であった。その他の試験結果は表 10 及び表 11 に示した。

【0091】上記のポリエステル系ウレタン樹脂溶液は、アジピン酸、ネオペンチルグリコール、1,6-ヘキサジオールから合成されたポリエステルポリオール 60 g、3-イソシアネートメチル-3,5,5-トリメチルシクロヘキシルイソシアネート 90 g、1,3-ビス (1-イソシアネート-1-メチルエチル) ベンゼン 30 g、ジメチロールプロピオン酸 40 g、トリエチレングリコール 5 g、2-[(2-アミノエチル) アミノ] エタノール 10 g を反応させた後、水酸化ナトリウ

#### 【0087】高分子の合成例 4

上記の合成例 1 において、ジメチルアクリルアミド 45 部、ベンジルメタクリレート 24 部、メタクリル酸 31 部、ラウリルメルカプタン 2 部の混合物を使用したこと以外は、合成例 1 と同様にして酸価が 200 mg KOH / g の高分子を得た。次いで、冷却下、水酸化ナトリウム水溶液をフラスコに滴下して中和した後、エタノールを除去し、アニオン性高分子 (D) 水溶液を得た。この高分子は、重量平均分子量が 11,500、高分子中に占めるアミド結合を有する単量体の割合が 48 モル%、高分子中に占める疎水基を有する単量体の割合が 14 モル%であった。

#### 【0088】実施例 1

次の表 6 に示す各成分を採取し、平均 0.6 mm 径のジルコニアビーズを使用しサンドグラインダーにて分散処理を行った。

#### 【0089】

#### 【表 6】

ムで中和することにより得られ、遊離酸の酸価: 70 mg KOH / g、Tg: 190°C、Mw: 20 万、固形分濃度: 25% である。

#### 【0092】実施例 2

実施例 1 と同様にして分散処理して得られた液に、酸価 70 のポリエステル系ウレタン樹脂溶液 9 部、グリセリン 9 部、2-ピロリドン 12.6 部、イソプロピルアルコール 3.6 部、イオン交換水 45.8 部を更に加えた。この液を No. 5C の濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は 0.137  $\mu\text{m}$  であり、記録液の表面張力は 48 dyne / cm であった。その他の試験結果は表 10 及び表 11 に示した。

#### 【0093】比較例 1

実施例 1 において、酸価 70 のポリエステル系ポリウレタン樹脂の代わりに、酸価 50 のポリエステル系ポリウレタン樹脂を使用した以外は、実施例 1 と同様にして記録液を調製し評価した。得られた記録液中のカーボンブラックの平均分散粒径は 0.138  $\mu\text{m}$  であり、記録液

の表面張力は34 dyne/cmであった。印字試験結果を表10に示すが、耐擦性試験は印字不良のために実施できなかった。

#### 【0094】比較例2

実施例2において、酸価70のポリエステル系ポリウレタン樹脂の代わりに、酸価50のポリエステル系ポリウレタン樹脂を使用した以外は、実施例1と同様にして記録液を調製し評価した。得られた記録液中のカーボンブラックの平均分散粒径は0.140 μmであり、記録液の表面張力は33 dyne/cmであった。印字試験結果を表10に示すが、耐擦性試験は印字不良のために実施できなかった。

#### 【0095】実施例3

成 分	使用量 (部)
カーボンブラック (A)	5
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」(酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	2.5
グリセリン	3
イオン交換水	53.5
合計	64

【0098】上記で得られた液に、前記合成例1で得た高分子(A)水溶液3.8部(高分子1.25部)、グリセリン5部、イソプロピルアルコール2部、2-ピロリドン7部、イオン交換水18.2部を更に加えた。この液をNo. 5Cの濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は0.143 μmであり、記録液の表面張力は50 dyne/cmであった。その他の試験結果は、その他の試験結果は表12に示した。

#### 【0099】実施例5

実施例4において、高分子(A)水溶液3.8部(高分子1.25部)の代わりに前記合成例2で得た高分子

実施例1において、カーボンブラック(A)の代わりに、カーボンブラック(B)を使用した以外は実施例1と同様に記録液を調製し、評価を行った。得られた記録液中のカーボンブラックの平均分散粒径は0.140 μmであり、記録液の表面張力は35 dyne/cmであった。その他の試験結果は表10及び表11に示した。

#### 【0096】実施例4

次の表7に示す各成分を採取し、平均0.6mm径のジルコニアビーズを使用しサンドグラインダーにて分散処理を行った。

#### 【0097】

#### 【表7】

(B)水溶液3.8部(高分子1.25部)を使用したこと以外は、実施例4と同様にして記録液を得た。得られた記録液中のカーボンブラックの平均分散粒径は0.138 μmであり、記録液の表面張力は50 dyne/cmであった。その他の試験結果は表12に示した。

#### 【0100】実施例6

次の表8に示す各成分を採取し、平均0.6mm径のジルコニアビーズを使用しサンドグラインダーにて分散処理を行った。

#### 【0101】

#### 【表8】

成 分	使用量 (部)
カーボンブラック (A)	4
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」(酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	2.0
グリセリン	3
イオン交換水	42.2
合計	51.2

【0102】上記で得られた液に、前記合成例2で得た高分子(B)水溶液6.1部(高分子2.0部)、グリ

セリン5部、イソプロピルアルコール2部、2-ピロリドン7部、イオン交換水28.7部を更に加えた。この液をNo. 5Cの濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は $0.139\mu\text{m}$ であり、記録液の表面張力は $48\text{dyne/cm}$ であった。その他の試験結果は表12に示した。

#### 【0103】実施例7

実施例6と同様にして得た分散液に、前記合成例3で得た高分子(C)水溶液4.1部(高分子1.0部)、グリセリン5部、イソプロピルアルコール2部、2-ピロリドン7部、イオン交換水30.7部を更に加えた。この液をNo. 5Cの濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は $0.311\mu\text{m}$ であり、記録液の表面張力は $52\text{dyne/cm}$ であった。その他の試験結果はその他の試験結果は表12に示した。

#### 【0104】実施例8

実施例6と同様にして得た分散液に、前記合成例4で得た高分子(D)水溶液4.7部(高分子1.6部)、グリセリン5部、イソプロピルアルコール2部、2-ピロリドン7部、イオン交換水30.1部を更に加えた。この液をNo. 5Cの濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は $0.176\mu\text{m}$ であり、記録液の表面張力は $51\text{dyne/cm}$ であった。その他の試験結果は表12に示した。

#### 【0105】実施例9

実施例6と同様にして得た分散液に前記合成例2で得た高分子(B)水溶液3.8部(高分子1.25部)、グ

リセリン5部、トリエチレングルコールモノブチルエーテル4.0部、2-ピロリドン7部、イオン交換水39部を更に加えた。この液をNo. 5Cの濾紙で加圧濾過し、ここで得られた液を記録液とした。得られた記録液中のカーボンブラックの平均分散粒径は $0.114\mu\text{m}$ であり、記録液の表面張力は $44\text{dyne/cm}$ であった。その他の試験結果は表12に示した。

#### 【0106】

【表9】

	MCマット紙 (Epson 社製品)
受容層の平均細孔孔 ( $\mu\text{m}$ )	4.85
S. A. D	93.4

#### 【0107】

【表10】

	印字試験	印字濃度
実施例1	○	1.6
実施例2	△	—
実施例3	○	1.4
比較例1	×	—
比較例2	×	—

(試験に供した記録紙: MCマット紙)

#### 【0108】

【表11】

		実施例1	実施例2	実施例3
マット紙	MCマット紙 (Epson 社製品)	○	—	○
	MJ A 4 SP 1 (Epson 社製品)	○	—	○
光沢紙	HG 2 0 1 (Canon 社製品)	○	—	○
	HG 1 0 1 (Canon 社製品)	○	—	○
	MJ A 4 SP 6 (Epson 社製品)	○	—	○
	C 6 0 4 3 A (ヒューレットパッカート 社製品)	○	—	○
普通紙	Xerox 4 0 2 4 (Xerox 社製品)	○	○	○
	Xerox 4 2 0 0 (Xerox 社製品)	○	○	○

#### 【0109】

【表12】

	印字試験	印字濃度	耐マーカ性
実施例 4	○	1. 5 9	△
実施例 5	○	1. 5 5	△
実施例 6	○	1. 4 0	○
実施例 7	○	1. 5 3	△
実施例 8	○	1. 4 3	○
実施例 9	○	1. 2 8	○

(試験に供した記録紙：Xerox 4 0 2 4)

# 【0110】

【発明の効果】以上説明した本発明によれば、保存安定性や吐出性に優れ、特にインクジェット記録用または筆

記具用として普通紙に記録した場合にも、記録物の印字濃度、耐擦性、耐水性および耐光性などに優れる記録液が提供される。

フロントページの続き

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BC09 BC10 BC13 BC14 BC15  
BE01 BE22 EA35 EA36 EA38  
EA41 EA44 EA46 FA02 GA24  
GA27

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**CLAIMS**

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**[Claim(s)]**

- [Claim 1] Recording ink which has one or more association chosen from a pigment (a) and the group which changes from amide association, a urethane bond, and urea association to intramolecular at least, and contains the macromolecule (b) whose acid number of the free acid is 55 – 350 mgKOH/g, and is characterized by surface tension being 25 – 54 dyne/cm.
- [Claim 2] Recording ink according to claim 1 whose acid number of the free acid of a macromolecule (b) is 55 or more mgKOH/g less than 150 mgKOH/g.
- [Claim 3] Recording ink according to claim 2 whose macromolecule (b) is urethane system resin.
- [Claim 4] Recording ink according to claim 1 whose acid number of the free acid of a macromolecule (b) is 100 – 350 mgKOH/g.
- [Claim 5] Recording ink according to claim 4 which is the polymer with which a macromolecule (b) makes an acrylamide derivative and/or a methacrylamide derivative a part of configuration unit.
- [Claim 6] Recording ink according to claim 1 whose surface tension of recording ink is 25 or more dyne/cm less than 37 dyne/cm.
- [Claim 7] Recording ink according to claim 6 whose macromolecule (b) is urethane system resin.
- [Claim 8] Recording ink according to claim 1 whose surface tension of recording ink is 37 or more dyne/cm less than 54 dyne/cm.
- [Claim 9] Recording ink of the \*\*\*\*\* 8 publication which is the polymer with which a macromolecule (b) makes an acrylamide derivative and/or a methacrylamide derivative a part of configuration unit.
- [Claim 10] Recording ink according to claim 1 whose surface tension of recording ink the acid number of the free acid of a macromolecule (b) is 55 – 150 mgKOH/g, and is 25 or more dyne/cm less than 37 dyne/cm.
- [Claim 11] Recording ink according to claim 10 whose macromolecule (b) is urethane system resin.
- [Claim 12] Recording ink of claim 1 whose surface tension of recording ink the acid number of the free acid of a macromolecule (b) is 100 – 350 mgKOH/g, and is 37 – 54 dyne/cm.
- [Claim 13] Recording ink according to claim 12 which is the polymer with which a macromolecule (b) makes an acrylamide derivative and/or a methacrylamide derivative a part of configuration unit.
- [Claim 14] Recording ink containing anionic water soluble polymers other than a macromolecule (b) according to claim 1.
- [Claim 15] Recording ink according to claim 14 whose acid number of anionic water soluble polymers other than a macromolecule (b) is 150 or more mg-KOH/g.
- [Claim 16] Recording ink according to claim 14 whose anionic water soluble polymers are styrene (alpha-methyl) / (meta) acrylic-acid copolymer.
- [Claim 17] Recording ink according to claim 1 whose pigment (a) is carbon black.
- [Claim 18] Recording ink according to claim 17 whose DBP oil absorption of carbon black is 100cm<sup>3</sup>/100g or more.
- [Claim 19] Recording ink according to claim 1 which contains a non-ion system surfactant 0.5 to 50% of the weight.
- [Claim 20] The ink jet record approach characterized by what is recorded on the sheet for record which an ink absorbing layer is established at least in one side of a base material, and changes using

recording ink according to claim 1

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the recording ink suitable for the recording ink for ink jets, or the recording ink for writing implements, and the ink jet record approach especially in detail about recording ink.

[0002]

[Description of the Prior Art] Conventionally, the solvent system recording ink which dissolved the aqueous recording ink (ink) by which acid dye and direct dye were dissolved into the aqueous medium, and an oil color into the organic solvent as recording ink for ink jet record (ink jet recording ink) has been used. Solvent system recording ink has a problem by the environmental safety aspect, in order to use a solvent, and the application is limited to use in office, a home, etc. by the not suitable reason. In the most common aqueous recording ink used for the object for office, or an ink jet printer for home use, since water-soluble coloring matter (color) is used, there is a problem that the water resisting property of a printing object and lightfastness are inadequate. And such a thing is the same not only about ink jet recording ink but the recording ink for writing implements.

[0003] In order to solve the above-mentioned problem, the recording ink which distributed pigments, such as carbon black which is excellent in a water resisting property and lightfastness as a color material, is partly used into the aqueous medium, but especially, conventional recording ink is inadequate in respect of the scuff resistance of a printing object, and when a printing object is ground against a fluorescence marker etc., it has problems, such as producing dirt.

[0004] Although the recording ink which added various macromolecules as a binder is examined in order to solve the above-mentioned problem, regurgitation stability is spoiled by the reasons of a rise of viscosity etc. and the recording ink with which are satisfied of all the regurgitation stability of recording ink, the printing concentration of a printing object, the scuff resistance, and marker-proof nature is not yet obtained as a result. Especially when aiming at a notice of a printing object etc., the record approach recorded on support surfaces, such as paper and a resin film, with an ink jet method to the exclusive record sheet possessing an ink absorbing layer is being adopted. In this case, when it is going to acquire good dischargeability and preservation stability, there is a problem which becomes inadequate [ the so-called glossy paper with a smooth front face / the scuff resistance of a printing object or gloss ], and becomes inadequate [ the so-called high mat paper of surface roughness / the printing concentration of a printing object ].

[0005]

[Problem(s) to be Solved by the Invention] It is in offering the recording ink which this invention is made in view of the above-mentioned actual condition, and the purpose is excellent in preservation stability or dischargeability, and is especially excellent in the printing concentration of a printing object, scuff resistance, marker-proof nature, a water resisting property, lightfastness, etc. also when it records on exclusive glossy paper, exclusive mat paper, a regular paper, etc. as the object for ink jet record, or an object for writing implements. Moreover, other purposes of this invention are to offer the ink jet record approach which used the above-mentioned recording ink.

[0006]

[Means for Solving the Problem] As a result of examining many things, by making pigment-content



powder recording ink contain a specific macromolecule, and making the range of the surface tension of the recording ink concerned optimize, this invention persons acquired knowledge that the above-mentioned purpose can be attained easily, and resulted in completion of this invention.

[0007] That is, the 1st summary of this invention has one or more association chosen from a pigment (a) and the group which changes from amide association, a urethane bond, and urea association to intramolecular at least, and contains the macromolecule (b) whose acid number of the free acid is 55 – 350 mgKOH/g, and consists in the recording ink characterized by surface tension being 25 – 54 dyne/cm. And the 2nd summary of this invention consists in the ink jet record approach characterized by what is recorded on the sheet for record which an ink absorbing layer is established at least in one side of a base material, and changes using the above-mentioned recording ink.

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. First, the pigment (a) used by this invention is explained. In this invention, you may be any of an organic pigment and an inorganic pigment, and these examples are as follows.

[0009] As a pigment used for yellow ink, the C.I. pigment yellow 1, 2, 3, 12, 13, 14, 16, 17, 73, 74, 75, 83, 93, 95, 97, 98, 114, 128, 129, and 151 and 154 grades are mentioned. As an example of the pigment used for Magenta ink, the C.I. pigment red 5, 7, and 12, 48(calcium) C.I.48(Mn), 57 (calcium), 57:1, 112, 123, 168 and 184, and 202 grades are mentioned. As an example of the pigment used for cyanogen ink, the C.I. pigment blues 1, 2, 3, 15:3, 15:34, 16, 22, 60, and 4 and 60 grades are mentioned.

[0010] The C.I. pigment [ besides above ] red 209, 122, 224, 177, and 194, C.I. pigment Orange 43, the C.I. bat violet 3, the C.I. pigment violet 19, 23, and 37, C.I. pigment Green 36 and 7, the C.I. pigment blue 15:6, and 209 grades can also be used.

[0011] moreover, this invention — if it is, various kinds of carbon black, such as acetylene black, channel black, and furnace black, can be used as a pigment. In these, channel black or furnace black is desirable, and especially furnace black is desirable.

[0012] although the DBP oil absorption of the above-mentioned carbon black is usually 60ml / 100g or more from the viewpoint of printing concentration — desirable — 100ml/— 100g or more is 140ml / 100g or more still more preferably. Volatile matter is usually 4 or less % of the weight preferably 8 or less % of the weight. although pH is usually set to 1–14 — from a viewpoint of the preservation stability of recording ink — desirable — 3–11 — it is 6–9 still more preferably. although a BET specific surface area is usually carried out to more than 100m<sup>2</sup>/g — desirable — 150–600m<sup>2</sup>/g — < — it is 260–500m<sup>2</sup>/g still more preferably. Although primary particle diameter is usually set to 30nm or less, it is 15nm or less especially preferably 16nm or less still more preferably 20nm or less preferably. Here, DBP oil absorption is JIS. K6221 The value and volatile matter which were measured by A law are JIS. The value and primary particle diameter which were measured by the approach of K6221 are an arithmetic mean diameter (number average) by the electron microscope.

[0013] As an example of the above carbon black, "Color BlackFW1", "FW2", "FW2V", "FW18", "FW200", "SpecialBlack 6", "Color Black S170" (above Degussa product), "CONDUCTEX975ULTRA" (colon BIAN product), etc. are mentioned.

[0014] Moreover, in this invention, the things (graft-ized processing, thing made to adsorb beforehand before distributing a dispersant) which combined physically or chemically the things (oxidation treatment, fluorination processing, etc.) and dispersant which processed the above-mentioned pigment chemically, the surfactant, etc. can be used. As an example of such a thing, Cab-o-jet 200 or Cab-o-jet300 (above the Cabot Corp. make, a trade name) is mentioned. In this invention, carbon black is suitably used especially in the pigment mentioned above.

[0015] Next, it has one or more association chosen from the group which is used by this invention, and which changes from amide association, a urethane bond, and urea association to intramolecular, and the macromolecule (b) whose acid number of a free acid is 55 – 350 mgKOH/g is explained.

[0016] The giant molecule compounded so that it might have amide association in intramolecular, it might have amide association in a principal chain besides the giant molecule obtained by carrying out the polymerization of the unit which has amide association of acrylamide (meta), vinyl pyrrolidone, etc., for example as a giant molecule whose acid number of a free acid is 55 – 350 mgKOH/g, and the

unit which has acid radicals, such as an acrylic acid (meta), and it might have an acid radical in a side chain is mentioned. As for these macromolecules, it is desirable to use it as a copolymer with other configuration units in respect of scuff resistance and marker-proof nature. The macromolecule which has a hydrophobic radical especially is desirable. In addition, the above-mentioned acrylamide (meta) points out the thing of methacrylamide and/or acrylamide, and an acrylic acid (meta) points out a methacrylic acid and/or an acrylic acid.

[0017] The organic radical which has rings, such as a phenyl group which may be permuted, benzyl, and a naphthyl group, as the above-mentioned hydrophobic radical, the alkyl group which are four or more carbon numbers, and may be branched or permuted, an alkenyl radical, an alkynyl group, a cycloalkyl radical, etc. are mentioned. Especially, the organic radical on which a carbon number has the organic radical and/or ring of 4-10 is desirable. As an example of a monomer of having a hydrophobic group, styrene, benzyl (meta) acrylate, ethylhexyl (meta) acrylate, hexyl (meta) acrylate, butyl (meta) acrylate, etc. are mentioned.

[0018] Moreover, as an example of a giant molecule (b) in which the acid number of a free acid is 100 - 350 mgKOH/g, acrylamide / ethylhexyl methacrylate / methacrylic-acid copolymer, dimethyl acrylamide / benzyl methacrylate / methacrylic-acid copolymer, diacetone acrylamide / methyl methacrylate / butyl acrylate / methacrylic-acid copolymer, methacrylamide / styrene / acrylic-acid copolymer, etc. are mentioned especially.

[0019] As an example of a monomer of having amide association, although an acrylamide derivative, methacrylamide derivatives, etc., such as diethyl acrylamide, propyl acrylamide, diisopropyl methacrylamide, and diacetone acrylamide, can be used in addition to acrylamide, methacrylamide, and dimethyl acrylamide, acrylamide, methacrylamide, dimethyl acrylamide, dimethyl methacrylamide, monomethyl acrylamide, and monomethyl methacrylamide are desirable in respect of preservation stability and regurgitation stability.

[0020] the rate of a monomer of having amide association in a macromolecule — from a viewpoint of scuff resistance and dischargeability — usually — more than 10mol% — it is 10-50-mol% preferably. the rate of the hydrophobic monomer in a macromolecule — from a viewpoint of marker-proof nature — usually — more than 10mol% — desirable — more than 20mol% — it is 20-mol% - 70-mol% still more preferably. the monomer which has amide association in a macromolecule — comparatively (mol%) — the ratio (mol%) of the rate of a hydrophobic monomer — from a viewpoint of preservation stability and dischargeability — usually — it is 1/3 or more still more preferably 1/5 or more preferably 1/15 or more.

[0021] Have a urethane bond in intramolecular and as a macromolecule whose acid number of a free acid is 55 - 350 mgKOH/g Mainly For example, a diisocyanate compound and diol compounds, such as polyether diols, polyester diols, and polycarbonate diols, various kinds of urethane system resin (aliphatic series system urethane resin —) water-soluble [ which is reacted and acquired in acid radical content diols, such as a carboxylic-acid radical and a sulfonic group, ], or water-dispersion Aromatic series system urethane resin, ester system urethane resin, ether system urethane resin, carbonate system urethane resin, etc. are mentioned.

[0022] As the above-mentioned diisocyanate, for example Hexamethylene di-isocyanate, Aliphatic series diisocyanate compounds, such as hexamethylene di-isocyanate, 2 and 2, and 4-trimethyl hexamethylene di-isocyanate, Isophorone diisocyanate, hydrogenation xylylene diisocyanate, 1, 4-cyclohexane diisocyanate, Cycloaliphatic diisocyanate compounds, such as 4 and 4'-dicyclohexylmethane diisocyanate, Aroma aliphatic series diisocyanate compounds, such as xylylene diisocyanate and tetramethyl xylenediisocyanate, Aromatic series diisocyanate compounds, such as toluylene di-isocyanate and phenylmethane diisocyanate, the denaturation objects (a carbodiimide, urethodione, URETO imine content conversion object, etc.) of these diisocyanate, etc. are mentioned.

[0023] With the above-mentioned diol compound, poly lactone diols, such as polyester diols, such as polyether diols, such as a polyethylene glycol, a polypropylene glycol, a polytetramethylene ether glycol, and polyhexamethylene ether glycol, a polyethylene horse mackerel peat, a polybutylene horse mackerel peat, a poly neopentyl horse mackerel peat, a Polly 3-methyl pentyl horse mackerel peat, polyethylene / butylene horse mackerel peat, and poly neopentyl / hexyl horse mackerel peat, and the poly caprolactone diol, and polycarbonate diol are mentioned. The diol compound of a polyether

system or a polyester system is especially desirable.

[0024] As the above-mentioned acid radical content diol, a dimethylol acetic acid, dimethylol propionic acid, dimethylol butanoic acid, etc. are mentioned, for example. Especially dimethylol propionic acid is desirable.

[0025] Urethane system resin may be compounded by the prepolymer method, and may use the polyhydroxy compound of low molecular weight in that case. As a polyhydroxy compound of low molecular weight, trihydric alcohol, such as a glycol mentioned as a raw material of the above-mentioned polyester diol and an alkylene oxide low mol addition product, a glycerol, trimethylolethane, and trimethylol propane, the alkylene oxide low mol addition product of those, etc. are mentioned.

[0026] moreover — while neutralizing an urethane prepolymer after it neutralizes the acid radical originating in a dimethylol alkane acid or — water extension — or JI or triamine extension can be carried out. As polyamine used in the case of amine extension, diamine or triamine is usually mentioned. Moreover, a hexamethylenediamine, isophorone diamine, a hydrazine, a piperazine, etc. are mentioned as the example. As a base used in the case of the above-mentioned neutralization, inorganic bases, such as alkanolamines, such as alkylamines, such as a butylamine and triethylamine, monoethanolamine, diethanolamine, and triethanolamine, a morpholine, ammonia, and a sodium hydroxide, are mentioned, for example.

[0027] It has urea association in intramolecular, and the giant molecule whose acid number of a free acid is 55 – 350 mgKOH/g can be obtained by the above-mentioned water extension, JI, or triamine extension as a giant molecule which has a urethane bond and urea association. Moreover, in the case of the giant molecule which has only urea association in intramolecular, it can obtain by the reaction of diisocyanate and acid radical content diamine.

[0028] In this invention, as a macromolecule (b), urethane system resin is desirable and the urethane resin of an ester system, an ether system, or an aromatic series system is desirable especially. Each above-mentioned giant molecule (b) can be used in forms, such as organic amine salts, such as alkali-metal salts, such as Li, Na, and K, ammonia, dimethylamine, and ethanolamine (monochrome, JI, Tori).

[0029] Although the acid number of the free acid of the above-mentioned macromolecule (b) used by this invention is 55 – 350 mgKOH/g as above-mentioned, from a viewpoint which raises further the preservation stability and regurgitation stability of recording ink, the minimums of the acid number are 65 mgKOH/g still more preferably 60 mgKOH/g preferably, and the upper limits of the acid number are 300 mgKOH/g still more preferably 330 mgKOH/g preferably. Moreover, the acid number of the free acid of the macromolecule (b) which can be used for the application (for example, for desktops) for which a regular paper (and chiefly form) is used is 100 – 350 mgKOH/g preferably. Furthermore, the minimums of the acid number in this case are 150 mgKOH/g still more preferably 120 mgKOH/g preferably, and the upper limits of the acid number are 300 mgKOH/g still more preferably 330 mgKOH/g preferably. The acid number of the free acid of the macromolecule (b) which can be used for the application (for example, for a large format) for which only a form is used chiefly on the other hand is 55 – 150 mgKOH/g preferably. Furthermore, the minimums of the acid number in this case are 65 mgKOH/g still more preferably 60 mgKOH/g preferably, and the upper limits of the acid number are 100 mgKOH/g still more preferably 130 mgKOH/g preferably. moreover, the weight average molecular weight of the above-mentioned macromolecule (b) — from a viewpoint of regurgitation stability — usually — 300,000 or less — desirable — 5000–45,000 — further — desirable — 5000–30,000 — it is 5000–20,000 especially preferably.

[0030] Various additives can be used for the recording ink concerning this invention, for example, various kinds of anionic detergents, the Nonion nature surfactant, a cationic surfactant, an amphoteric surface active agent, a water soluble polymer, etc. are mentioned.

[0031] As an anionic detergent, fatty-acid salts, alkyl-sulfuric-acid ester salts, Alkylbenzene sulfonates and alkyl naphthalenesulfonate Alkyl sulfo succinate and alkyl diphenyl ether disulfon acid chloride Alkyl phosphate, polyoxyethylene alkyl-sulfuric-acid ester salts, Polyoxyethylene alkyl aryl sulfate salts and alkane sulfonates naphthalene sulfonic-acid formalin condensates, polyoxyethylene alkyl phosphoric ester, and N-methyl-N-me — oil taurine acid chloride and alpha olefin sulfonates are mentioned.

[0032] Especially as a nonionic surfactant, although not restricted, what has ethyleneoxide structure

or propylene oxide structure from the point of preservation stability and printing concentration is desirable, and the thing of 9-17, especially 10-16 has still more desirable HLB also in it.

[0033] As an example of a nonionic surfactant, the polyoxyethylene nonylphenyl ether, Polyoxyethylene octyl phenyl ether, polyoxyethylene alkyl ether, The polyoxyethylene lauryl ether, the polyoxyethylene oleyl ether, The polyoxyethylene tridecyl ether, the polyoxyethylene cetyl ether, Polyoxyethylene stearyl ether, polyoxyethylene alkylamine, An amino polyoxyethylene, a sorbitan fatty acid ester, polyoxyethylenesorbitanlaurate, Polyoxyethylene sorbitan palmitate, polyoxyethylene sorbitan stearate, Polyoxyethylene sorbitan oleate, a naphthol ethylene oxide addition product, An acetylene glycol ethylene oxide addition product, a bisphenol A ethylene oxide addition product, Oxyethylene oxypropylene block polymer, a sorbitan fatty acid ester, Polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, etc. are mentioned.

[0034] On the other hand, as a cationic surfactant and an amphoteric surface active agent, alkylamine salts, quarternary ammonium salt, alkyl betaines, and amino KISAIDO are mentioned.

[0035] In addition, the other various water soluble polymers may be used together with the aforementioned macromolecule (b).

[0036] As an anionic water soluble polymer, 200 or more mgKOH/g of acid numbers in the form of the viewpoint of preservation stability of recording ink to a free acid is 150 or more mgKOH/g usually still more preferably suitable for the thing of 250 or more mgKOH/g preferably. Furthermore, the copolymer which has a hydrophobic radical is desirable in respect of the distributed stability of carbon black, the water resisting property of a printing object, and scuff resistance.

[0037] Although the organic radical which has rings, such as a phenyl group which may be permuted, benzyl, and a naphthyl group, as a hydrophobic radical in a giant molecule, the alkyl group which are four or more carbon numbers, and may be branched or permuted, an alkenyl radical, an alkynyl group, a cycloalkyl radical, etc. are mentioned, the organic radical which has a ring especially is desirable.

[0038] As an anionic water soluble polymer used by this invention Specifically Styrene (alpha-methyl) / maleic-acid copolymer, styrene (alpha-methyl) / (meta) acrylic-acid copolymer, That it is \*\*\*\* in styrene / (meta) acrylic ester / (meta) acrylic-acid copolymer, acrylic ester (meta) / (meta) acrylic-acid copolymer, acrylic ester (meta) / maleic-acid copolymer, and/or these (alpha-methyl) \*\*\*\*\* They are styrene (alpha-methyl) / (meta) acrylic-acid copolymer preferably. Here, styrene (alpha-methyl) points out the thing of alpha methyl styrene and/or styrene, and an acrylic acid (meta) points out the thing of a methacrylic acid and/or an acrylic acid.

[0039] Moreover, although any of block polymer, a graft polymer, and a random polymer are sufficient as the anionic water soluble polymer used by this invention, a point to its graft polymer or random polymer of a manufacturing cost is desirable, and especially its random polymer is mainly desirable. Moreover, as for weight average molecular weight, 50,000 or less are desirable, 15,000 or less are still more desirable, and 10,000 especially or less are more desirable than the viewpoint of regurgitation stability. Furthermore, the acid number can use the copolymer of 150 or more mgKOH/g in forms, such as organic amine salts, such as alkali-metal salts, such as Li, Na, and K, ammonia, dimethylamine, and ethanolamine (monochrome, JI, Tori).

[0040] As a commercial item of the above giant molecules or a polymer solution, the "JON krill 67" by the Johnson polymer company, "678", "680", "682", "690" and/or its salt, the "JON krill 52", "57", "60", "62", "63", "70", "354", "501", "6610", etc. are mentioned.

[0041] Although the aqueous medium which makes water a subject is usually used as a medium of the recording ink of this invention, it is desirable to add and use a water-soluble organic solvent for water in this case.

[0042] As the water-soluble above-mentioned organic solvent, ethylene glycol, propylene glycol, 1, 3-propanediol, a butylene glycol, a diethylene glycol, triethylene glycol and a polyethylene glycol (example: — "#200" by Wako Pure Chem —) "#300", "#400", "#4000", "#6000", A glycerol, N-methyl pyrrolidone, 1, 3-dimethyl imidazolinone, Thiodiglycol, 2-pyrrolidone, a sulfolane, dimethyl sulfoxide, Diethanolamine, triethanolamine, methanol, ethanol, isopropanol, neopentyl alcohol, trimethylol propane, 2, and 2-dimethyl propanol etc. is mentioned.

[0043] In this invention, since the surface tension of recording ink is lowered and the osmosis rate to the space of ink and the rate of drying of a record object are raised, the Nonion nature surfactant of

low molecular weight can be used.

[0044] As an example of the Nonion nature surfactant of the above-mentioned low molecular weight Ethylene glycol monomethyl ether, ethylene glycol wood ether, Ethylene glycol monoethyl ether, ethylene glycol diethylether, The ethylene glycol mono—n-propyl ether, ethylene glycol mono—isopropyl ether, Ethylene glycol mono—n-butyl ether, ethylene glycol mono—sec-butyl ether, The ethylene glycol mono—isobutyl ether, ethylene glycol mono—tert-butyl ether, Ethylene glycol mono—n-amyl ether, the ethylene glycol mono—n-hexyl ether, Propylene glycol monomethyl ether, propylene glycol wood ether, The propylene glycol monoethyl ether, propylene glycol diethylether, The propylene glycol mono—n-propyl ether, propylene glycol mono—isopropyl ether, Propylene glycol mono—n-butyl ether, propylene glycol mono—sec-butyl ether, The propylene glycol mono—isobutyl ether, propylene glycol mono—tert-butyl ether, The diethylene-glycol monomethyl ether, diethylene-glycol wood ether, Diethylene glycol monoethyl ether, the diethylene-glycol mono—n-propyl ether, Diethylene-glycol mono—isopropyl ether, diethylene-glycol mono—n-butyl ether, Diethylene-glycol mono—sec-butyl ether, the diethylene-glycol mono—isobutyl ether, Diethylene-glycol mono—tert-butyl ether, dipropylene glycol monomethyl ether, The dipropylene glycol monoethyl ether, the dipropylene glycol mono—n-propyl ether, Dipropylene glycol mono—n-butyl ether, the polyethylene-glycol monopropyl ether, The polyethylene-glycol monobutyl ether, the ethylene glycol addition product of a glycerol (example: RIPONIKKU EG-1 (product made from RIPOKEMIKARU) etc.), The ethylene glycol addition product of acetylene glycols (example: SAFI Norian 440, SAFI Norian 465, SAFI Norian 485 (Nissin Chemical Industry make), ASECHIRE Norian EH, ASECHIRE Norian EL (above, Kawaken Fine Chemicals make), etc. are mentioned.)

[0045] the amount of the Nonion nature surfactant used of low molecular weight — the recording ink 100 weight section — receiving — usually — 0.5 – 50 weight section — desirable — 2 – 30 weight section — it is 5 – 20 weight section still more preferably. Although the surface tension of recording ink is appropriately controlled by the class and the amount of the Nonion system surfactant of the low molecular weight used, it is necessary to make surface tension of the recording ink of this invention into the range of 25 – 54 dyne/cm. As a result of osmosis of the recording ink to a recorded material becoming slow when it prints as recording ink if surface tension becomes larger than 54 dyne/cm, the fault that printing speed must be made late occurs. Moreover, in the range where the surface tension of recording ink is smaller than 25 dyne/cm, since osmosis of the recording ink to a recorded material becomes large too much, printing concentration is spoiled.

[0046] And by 25 or more dyne/cm less than 37 dyne/cm, urethane system resin is suitably used for the surface tension of recording ink as a macromolecule (b) the preservation stability of recording ink, and in respect of scuff resistance among the above-mentioned range. Moreover, when the surface tension of recording ink is 37 or more dyne/cm less than 54 dyne/cm, the polymer which makes an acrylamide derivative and/or a methacrylamide derivative a part of configuration unit is suitably used as a macromolecule (b).

[0047] When it sees from the class of print sheet, in the case of an application (for example, for desktops) which is used for the above-mentioned regular paper (and chiefly form), in respect of the printing concentration of recording ink mainly moreover, the surface tension of recording ink Preferably 37 or more dyne/cm Usually, 40 or more dyne/cm, It is the range of 40 – 50 dyne/cm preferably. Furthermore, moreover, in the case of the above-mentioned application (for example, for a large format) which is chiefly used only for a form 35 or less dyne/cm of surface tension of recording ink is less than 37 dynes [/cm ] usually the range of 30 – 35 dyne/cm still more preferably preferably in respect of printing concentration and printing speed.

[0048] Other additives, such as antiseptics besides the above, an antifungal agent, a germicide, pH regulator, and a urea, may be used for the recording ink of this invention if needed.

[0049] According to a well-known approach, the recording ink of this invention carries out distributed processing of the pigment (a) in a medium to the bottom of existence of the aforementioned macromolecule (b) and the required aforementioned addition component, and obtains high-concentration dispersion liquid. Subsequently It is obtained by the approach of carrying out distributed processing of the pigment (a) to the bottom of existence of a macromolecule (b) and the required aforementioned addition component in the method (the masterbatch method) of adding a medium to the obtained dispersion liquid, performing concentration adjustment, and preparing

recording ink, or a medium, and preparing recording ink. Since distributed processing is performed by high concentration, the above-mentioned masterbatch method is efficient.

[0050] Jet mills which can carry out grinding processing as a disperser as a disperser used for distributed processing, without using media besides a ball mill, a roll mill, and SANDOGURAINDOMIRU, such as a nano mizer and Altima IZA, are used. A jet mill with little contamination which originates in SANDOGURAINDOMIRU or media especially is desirable. In this invention, a filter or a centrifugal separator removes a big and rough particle after grinding and distributed processing by the above-mentioned disperser.

[0051] The amount of the pigment (a) used is 1 – 10 % of the weight usually 2 – 6 % of the weight still more preferably two to 8% of the weight preferably to all recording ink weight. It has one or more association chosen from the group which changes from amide association, a urethane bond, and urea association to intramolecular, and the amount of the macromolecule (b) used whose acid number is 55 – 350 mgKOH/g is 5 – 200 % of the weight usually 8 – 70 % of the weight still more preferably eight to 100% of the weight preferably to the weight of a pigment (a). Moreover, the amount of the water-soluble above-mentioned organic solvent used is comparatively carried out in recording ink from a viewpoint of the preservation stability of recording ink, and is 5 – 30 % of the weight usually 8 – 20% of the weight of the range still more preferably five to 20% of the weight preferably.

[0052] The range of 0.05–0.2 micrometers of mean particle diameter of the pigment in recording ink is 0.01–0.3 micrometers usually from a viewpoint of distributed stability, regurgitation stability, and record concentration 0.1–0.2 micrometers still more preferably preferably. As for the maximum grain size of a pigment, it is desirable from a viewpoint of distributed stability and regurgitation stability that it is 5 micrometers or less. Moreover, 5–60nm of standard deviation in the distributed particle size distribution of the pigment in recording ink is 70nm or less usually preferably set to 10–50nm still more preferably from a viewpoint of the preservation stability of recording ink, regurgitation stability, and record concentration.

[0053] However, let an above-mentioned mean-dispersion particle size and distributed particle size distribution be the value measured with the particle-size-distribution meter:Nikkiso [ Co., Ltd. ] Co., Ltd. product "the micro truck UPA150."

[0054] The recording ink of this invention cannot stop at the object for ink jets, and writing implements, but can also be used as recording ink of other applications. Especially the recording ink of this invention is suitable for ink jet record. And although chiefly divided roughly into a form, the recording ink of the multilayer structure which the ink absorbing layer is established in at least the regular paper of 1 layer structure to which a recorded material changes from a cellulose, a loading material, a sizing compound, etc., and one side of a base material, and changes which is this invention can be used for all recorded materials (a regular paper, recycled paper, the papers only for ink jets (coat paper, glossy paper, etc.), the films only for ink jets (a coated film, gloss film, etc.), OHP film, etc.).

[0055] Next, the ink jet record approach concerning this invention is explained. In this invention, all the types of an on demand method, continuous method, and piezo method, a thermal method, etc. of the ink jet record approach is employable.

[0056] In this invention, the sheet for record which an ink absorbing layer is established at least in one side of a base material, and changes is used.

[0057] As a base material, addition components, such as a binder, a sizing compound, a fixing agent, a yield improver, a cation-ized agent, and a paper reinforcing agent, are mixed in the principal component which consists of wood pulp and pigments, such as chemical pulp, mechanical pulp, and recycled pulp, and the stencil paper manufactured with various equipments, such as a Fortlinear paper machine, a cylinder machine, and a twin-wired paper machine, is used for it. Moreover, what prepared resin layers, such as polyolefine besides the art paper and coat paper which prepared the coat layer on stencil paper, and cast coated paper, can be used. Furthermore, you may be the film (or sheet) which consists of synthetic resin and such mixture, such as polyethylene, polypropylene, polyester, nylon, rayon, polyurethane, and polyethylene terephthalate. These base materials are suitably chosen in consideration of the application of the record purpose and a record image, adhesion with an ink absorbing layer, etc.

[0058] An ink absorbing layer is formed by applying the binder resin with which the non-subtlety

particle (white pigments) was distributed on the surface of the base material.

[0059] As a non-subtlety particle, precipitated calcium carbonate, whiting, a kaolin, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc sulfide, zinc carbonate, a satin white, aluminum silicate, diatomaceous earth, a calcium silicate, synthetic amorphous silica, an aluminum hydroxide, a lithopone, a zeolite, hydrated halloysite, a magnesium hydroxide, alumina sol, fumed silica, colloidal silica, etc. are mentioned, for example. Moreover, the colloidal silica covered with the cation modifier which consists of metal oxidization hydrates, such as an aluminum oxide hydrate, a zirconium dioxide hydrate, and a tin-oxide hydrate, can also be used. These non-subtlety particles may use two or more sorts together. In addition, since the mean particle diameter of a non-subtlety particle changes with glossy paper and mat papers, it is chosen from the suitable range, respectively.

[0060] As binder resin, for example, polyvinyl alcohol, vinyl acetate, Cellulosics, such as oxidization starch, etherification starch, a carboxymethyl cellulose, and hydroxyethyl cellulose, Conjugated diene system polymerization latexes, such as maleic-anhydride resin, a styrene-butadiene copolymer, and a methyl methacrylate-butadiene copolymer Acrylic polymerization latexes, such as a polymer (\*\*) of acrylic ester, (Meta) The functional-group denaturation polymerization latexes by functional-group content monomers, such as a carboxyl group of vinyl system polymerization latexes, such as an ethylene-vinyl acetate copolymer, and these various polymers Polymethylmethacrylate, polyurethane resin, a vinyl chloride vinyl acetate copolymer, Thermosetting synthetic resin, such as an unsaturated polyester resin besides a polyvinyl butyral, casein, gelatin, soybean protein, and silyl denaturation polyvinyl alcohol, an alkyd resin, melamine resin, and a urea-resin, is mentioned.

[0061] Moreover, in this invention, a cationic organic substance can be used together in order to raise fixable [ of the carbon black as a color material ]. As this cationic organic substance, amines, such as quarternary ammonium salt and alkylamine, and amides are mentioned, for example. Moreover, the giant molecule which has such cationic residue in a side chain can also be used as a cationic organic substance.

[0062] Furthermore, as other additives, a pigment agent, a thickener, a fluid amelioration agent, a defoaming agent, foam suppressor, a release agent, a foaming agent, a penetrating agent, a coloring color, a color pigment, a fluorescent brightener, an anti-oxidant, antiseptics, an antifungal agent, a deck-watertight-luminaire-ized agent, a humid paper reinforcing agent, etc. can be blended suitably.

[0063] formation of an ink absorbing layer is [ size press / various blade coaters, a roll coater, an air knife coater, bar coater, rod blade coater, curtain coater, short dwell coater, ] well-known — it is carried out by carrying out various equipment use.

[0064] As for an ink absorbing layer, it is desirable to form the porous layer. 1 micrometers or more of average pore size of a porous layer are 0.5 micrometers or more usually from the printing concentration of a printing object, and a viewpoint of scratch-proof nature 2 micrometers still more preferably preferably. Here, the scanning electron microscope photograph on the front face of a record sheet is taken for two or more scale factors, and after digitizing by the scanner inputting method, the arithmetic mean diameter (number average) which computed and searched for distribution of the diameter of circle (grade area circle diameter) which has an area equal to the area of each opening part extracted by computer image analysis is called average pore size.

[0065] The above-mentioned recording ink concerning this invention is [ as opposed to / especially / the sheet for record possessing the ink absorbing layer of the comparatively high mat tone of surface roughness ] useful. therefore, S.A.D. on the above-mentioned front face of an ink absorbing layer (Surface Area Difference) — usually — still more preferably is preferably taken or more for 70 60 or more 50 or more. In this case, the printing object which was extremely excellent in printing concentration and scratch-proof nature can be obtained.

[0066] Above-mentioned S.A.D. is one of the indexes showing surface roughness, and a surface specific surface area is specifically expressed and it defines as the following formula (I). In this invention, S.A.D. is measured and computed on the conditions shown in the following table 1.

However, in the area at the time of the area of all the triangles formed by three data points with which Si adjoined, and Pi projecting Si on XY flat surface, and sigmaSi, all the sums of si and sigmaPi (s) express all the sums of Pi among a formula (I).

[0067]

[Equation 1] 
$$S.A.D. = \left\{ \left( \frac{\sigma Si}{\sigma Pi} \right) - 1 \right\} \times 100 (\%)$$

[0068]

[Table 1] (Measuring method)

equipment: — Scanning Probe Microscope model: — Digital Instruments Shrine make NanoScope III Scanner: J-Head measurement field: — 1 micrometer x 1-micrometer pixel number: — 512 x 512 Scan Rate: 1.0 Hz measurement mode: — Tapping AFM probe: — digital INSU vine face company make NCH-W [0069]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples, unless the summary is exceeded. They are weight criteria unless especially the "section" and "%" have a notice in many following examples. Moreover, measurement and the evaluation approach of physical properties are as follows at the used carbon black list.

[0070]

[Table 2]

<カーボンブラック>

	窒素吸着比表面積 ( $\text{m}^2/\text{g}$ )	DBP吸油量 ( $\text{ml}/100\text{g}$ )	1次粒子径 ( $\text{nm}$ )
カーボンブラック (A)	290	150	14
カーボンブラック (B)	350	86	12

[0071] (1) Printing trial : the ink jet printer was filled up with recording ink, solid printing was carried out at the paper only for ink jet printers (mat paper, glossy paper), and/or a regular paper (copy paper), and the criteria of the following three-stage estimated.

[0072]

[Table 3] O : there is no printing omission and the printing object also with the good grace of the edge section was obtained.

\*\*: Although there is a printing omission faintly, it is satisfactory practically.

x: A printing omission is remarkable.

[0073] (2) Printing concentration evaluation : the concentration of the printing object obtained by the above-mentioned printing trial was measured using the Macbeth concentration meter (RD914). It was shown that printing concentration is so good that a numeric value is large, and when it was 1.5 or more, it judged with success.

[0074] (3) Scuff resistance trial : it set in the printing object obtained by the above-mentioned printing trial, after recording ink was dried and established, the printing solid section was lightly ground against the metal spoon, and the criteria of the following three-stage estimated the scuff resistance of recording ink.

[0075]

[Table 4]

O : there is no peeling of recording ink and a recorded material front face is not exposed.

\*\*: Although there is peeling of recording ink faintly, it is satisfactory practically.

x: Peeling of recording ink is remarkable.

[0076] (4) Marker-proof trial : in the printing object obtained by the above-mentioned printing trial, the alphabetic character section was traced with the commercial yellow fluorescence marker (ZEBRA product OPTEX) 24 hours after after a printing trial, and the criteria of the following three-stage estimated the marker-proof nature of ink.

[0077]

[Table 5] O : there is almost no dirt of the alphabetic character section ground with the marker.

\*\*: Although there is dirt of the alphabetic character section ground with the marker faintly, it is satisfactory practically.

x: The dirt of the alphabetic character section ground with the marker is remarkable.

[0078] (5) Distributed particle-size-distribution measurement : recording ink was diluted with ion exchange water, and distributed particle size distribution was measured with the particle-size-distribution plan (Nikkiso [ Co., Ltd. ] Co., Ltd. product "the micro truck UPA150").

[0079] (6) Measurement of the average pore size of an ink absorbing layer, and the mean particle



diameter of white pigments : first, the scanning electron microscope (SEM) photograph on the front face of a record sheet (one 150 times the scale factor after enlargement of this) was inputted by 360dpi from the scanner, computer image processing was performed and digital imaging was carried out. The value of 1 pixel corresponded to 0.465 micrometers. The 512x512-pixel image of six sheets was processed similarly, and a total of 1723 pores (opening section) were extracted. It asked for the diameter of circle (grade area circle diameter) which has area [ area / of each extracted pore ], and average pore size (number average value) was computed from the distribution. The measurement result about the paper only for ink jet records of marketing with which the printing trial was presented is shown in Table 9.

[0080] (7) Measurement of S.A.D. on the front face of an ink absorbing layer : it measured by the approach given in the text about five on the front face of an ink absorbing layer (five fields), and the average was adopted. The measurement result about the paper only for ink jet records of marketing with which the printing trial was presented is shown in Table 9.

[0081] (8) Surface tension measurement : record liquid junction side tension was measured using the UIRUHERUMI mold surface tension measurement machine "CBVP-Z" (consonance interface science company make).

[0082] The ethanol 200 section was put into the four-lot flask furnished with synthetic example 1 reflux condenser of a high molecular compound, a thermometer, the glass tube for nitrogen purges, and stirring equipment, the azobisisobutironitoriru(azobisisobutyronitril) 2 section was added, and reflux heating was carried out at 80 degrees C under the nitrogen air current. The mixture of the dimethyl acrylamide 25 section, the benzyl methacrylate 44 section, the methacrylic-acid 31 section, and the lauryl mercaptan 5 section was dropped at this reaction container for 2 hours. After dropping termination, the 0.5 sections of azobisisobutironitoriru were added and the polymerization was performed for 4 hours. Subsequently, ethanol was removed and the high molecular compound was obtained.

[0083] In order to measure the acid number of the above-mentioned high molecular compound, after taking 1g of samples and dissolving in the mixed solvent of water/ethanol (50g/50g), 0.1NKOH water solutions performed the neutralization titration. Titration is JIS. Carrying out to K0113 by the potentiometric titration approach of a publication, a terminal point is JIS. K0113 It was decided by the point-of-inflection method of a publication that it would be 5.2.2. The amount of KOH needed for titration was made into the acid number. Consequently, the acid number of the above-mentioned high molecular compound was 200 mgKOH/g.

[0084] Next, under cooling, the sodium-hydroxide water solution was dropped at the flask, and it neutralized. Subsequently, ethanol was removed and the anionic macromolecule A water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 7,000 and a macromolecule is 29. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 29-mol %.

[0085] In the synthetic example 1 of the synthetic example 2 above of a giant molecule, the acid number obtained the giant molecule of 200 mgKOH/g like the synthetic example 1 except having used the mixture of the dimethyl acrylamide 15 section, the benzyl methacrylate 54 section, the methacrylic-acid 31 section, and the lauryl mercaptan 5 section. Subsequently, under cooling, after dropping the sodium-hydroxide water solution at the flask and neutralizing, ethanol was removed and the anionic macromolecule (B) water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 7,500 and a macromolecule is 18. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 38-mol %.

[0086] In the synthetic example 1 of the synthetic example 3 above of a giant molecule, the acid number obtained the giant molecule of 200 mgKOH/g like the synthetic example 1 except having used the mixture of the dimethyl acrylamide 45 section, the benzyl methacrylate 24 section, and the methacrylic-acid 31 section. Subsequently, under cooling, after dropping the sodium-hydroxide water solution at the flask and neutralizing, ethanol was removed and the anionic macromolecule (C) water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 33,000 and a macromolecule is 48. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule

was 14-mol %.

[0087] In the synthetic example 1 of the synthetic example 4 above of a giant molecule, the acid number obtained the giant molecule of 200 mgKOH/g like the synthetic example 1 except having used the mixture of the dimethyl acrylamide 45 section, the benzyl methacrylate 24 section, the methacrylic-acid 31 section, and the lauryl mercaptan 2 section. Subsequently, under cooling, after dropping the sodium-hydroxide water solution at the flask and neutralizing, ethanol was removed and the anionic macromolecule (D) water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 11,500 and a macromolecule is 48. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 14-mol %.

[0088] Each component shown in Table 6 of the primary example was extracted, and the Sand grinder performed distributed processing using the zirconia beads of the diameter of an average of 0.6mm.

[0089]

[Table 6]

成 分	使用量 (部)
カーボンブラック (A)	9
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」 (酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	4.5
グリセリン	5
イオン交換水	81.5
合計	100

[0090] The polyester system urethane resin solution (Takeda Chemical Industries, Ltd. make) 21.6 section obtained by the below-mentioned approach, the glycerol 22.5 section, the diethylene-glycol monobutyl ether 22.5 section, and the ion-exchange-water 58.4 section were further added to the liquid obtained above. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.139 micrometers, and the surface tension of recording ink was 33 dyne/cm. Other test results were shown in Table 10 and 11.

[0091] The above-mentioned polyester system urethane resin solution is polyester polyol 60g compounded from an adipic acid, neopentyl glycol, and 1,6-hexandiol, and 3-isocyanate methyl. - It is neutralizing by the sodium hydroxide, after making 3, 5, and 5-trimethyl cyclohexyl isocyanateg [ 90 ] and 1 and 3-screw (1-isocyanate-1-methylethyl) benzene 30g, 40g [ of dimethylol propionic acid ], and triethylene glycol 5g, and 2-[(2-aminoethyl) amino] ethanol 10g react. Acid-number:70 mgKOH/g which it is obtained and is a free acid, Tg:190 degree C, Mw: They are 200,000 and solid content concentration:25%.

[0092] The polyester system urethane resin solution 9 section of the acid number 70, the glycerol 9 section, the 2-pyrrolidone 12.6 section, the isopropyl alcohol 3.6 section, and the ion-exchange-water 45.8 section were further added to the liquid obtained by carrying out distributed processing like example 2 example 1. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.137 micrometers, and the surface tension of recording ink was 48 dyne/cm. Other test results were shown in Table 10 and 11.

[0093] In example of comparison 1 example 1, recording ink was prepared and evaluated like the example 1 instead of the polyester system polyurethane resin of the acid number 70 except having used the polyester system polyurethane resin of the acid number 50. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.138 micrometers, and the surface tension of recording ink was 34 dyne/cm. Although the printing test result was shown in Table 10, the scuff

resistance trial was not able to be carried out because of poor printing.

[0094] In example of comparison 2 example 2, recording ink was prepared and evaluated like the example 1 instead of the polyester system polyurethane resin of the acid number 70 except having used the polyester system polyurethane resin of the acid number 50. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.140 micrometers, and the surface tension of recording ink was 33 dyne/cm. Although the printing test result was shown in Table 10, the scuff resistance trial was not able to be carried out because of poor printing.

[0095] In example 3 example 1, it evaluated by preparing recording ink like an example 1 instead of carbon black (A) except having used carbon black (B). The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.140 micrometers, and the surface tension of recording ink was 35 dyne/cm. Other test results were shown in Table 10 and 11.

[0096] Each component shown in Table 7 of the 4th example was extracted, and the Sand grinder performed distributed processing using the zirconia beads of the diameter of an average of 0.6mm.

[0097]

[Table 7]

成 分	使用量 (部)
カーボンブラック (A)	5
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」 (酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	2.5
グリセリン	3
イオン交換水	53.5
合計	64

[0098] The (Macromolecule A) water-solution 3.8 section (macromolecule 1.25 section) obtained in said synthetic example 1, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 18.2 section were further added to the liquid obtained above. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.143 micrometers, and the surface tension of recording ink was 50 dyne/cm. Other test results showed other test results in Table 12.

[0099] In example 5 example 4, recording ink was obtained like the example 4 except having used the (Macromolecule B) water-solution 3.8 section (macromolecule 1.25 section) obtained in said synthetic example 2 instead of the (Macromolecule A) water-solution 3.8 section (macromolecule 1.25 section). The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.138 micrometers, and the surface tension of recording ink was 50 dyne/cm. Other test results were shown in Table 12.

[0100] Each component shown in Table 8 of the 6th example was extracted, and the Sand grinder performed distributed processing using the zirconia beads of the diameter of an average of 0.6mm.

[0101]

[Table 8]

成 分	使用量 (部)
カーボンブラック (A)	4
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」(酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	2.0
グリセリン	3
イオン交換水	42.2
合計	51.2

[0102] The (Macromolecule B) water-solution 6.1 section (macromolecule 2.0 section) obtained in said synthetic example 2, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 28.7 section were further added to the liquid obtained above. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.139 micrometers, and the surface tension of recording ink was 48 dyne/cm. Other test results were shown in Table 12.

[0103] The (Macromolecule C) water-solution 4.1 section (macromolecule 1.0 section) obtained in said synthetic example 3, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 30.7 section were further added to the dispersion liquid obtained like example 7 example 6. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.311 micrometers, and the surface tension of recording ink was 52 dyne/cm. Other test results showed other test results in Table 12.

[0104] The (Macromolecule D) water-solution 4.7 section (macromolecule 1.6 section) obtained in said synthetic example 4, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 30.1 section were further added to the dispersion liquid obtained like example 8 example 6. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.176 micrometers, and the surface tension of recording ink was 51 dyne/cm. Other test results were shown in Table 12.

[0105] The (giant-molecule B) water-solution 3.8 section (giant-molecule 1.25 section) obtained in said synthetic example 2, the glycerol 5 section, the TORIECHIREN glucol monobutyl ether 4.0 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 39 section were further added to the dispersion liquid obtained like example 9 example 6. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.114 micrometers, and the surface tension of recording ink was 44 dyne/cm. Other test results were shown in Table 12.

[0106]

[Table 9]

	MC マット紙 (Epson 社製品)
受容層の平均細孔 ( $\mu\text{m}$ )	4.85
S. A. D	93.4

[0107]

[Table 10]

	印字試験	印字濃度
実施例 1	○	1. 6
実施例 2	△	—
実施例 3	○	1. 4
比較例 1	×	—
比較例 2	×	—

(試験に供した記録紙：MCマット紙)

[0108]

[Table 11]

		実施例 1	実施例 2	実施例 3
マット紙	MC マット紙 (Epson 社製品)	○	—	○
	MJ A 4 SP 1 (Epson 社製品)	○	—	○
光沢紙	H G 2 0 1 (Canon 社製品)	○	—	○
	H G 1 0 1 (Canon 社製品)	○	—	○
	MJ A 4 SP 6 (Epson 社製品)	○	—	○
	C 6 0 4 3 A (ヒューレット・パッカート 社製品)	○	—	○
普通紙	Xerox 4 0 2 4 (Xerox 社製品)	○	○	○
	Xerox 4 2 0 0 (Xerox 社製品)	○	○	○

[0109]

[Table 12]

	印字試験	印字濃度	耐マーカ性
実施例 4	○	1. 5 9	△
実施例 5	○	1. 5 5	△
実施例 6	○	1. 4 0	○
実施例 7	○	1. 5 3	△
実施例 8	○	1. 4 3	○
実施例 9	○	1. 2 8	○

(試験に供した記録紙：Xerox 4 0 2 4)

[0110]

[Effect of the Invention] Also when according to this invention explained above it excels in preservation stability or dischargeability and records on a regular paper especially as the object for ink jet record, or an object for writing implements, the recording ink which is excellent in the printing concentration of a record object, scuff resistance, a water resisting property, lightfastness, etc. is offered.

[Translation done.]

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the recording ink suitable for the recording ink for ink jets, or the recording ink for writing implements, and the ink jet record approach especially in detail about recording ink.

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PRIOR ART

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[Description of the Prior Art] Conventionally, the solvent system recording ink which dissolved the aqueous recording ink (ink) by which acid dye and direct dye were dissolved into the aqueous medium, and an oil color into the organic solvent as recording ink for ink jet record (ink jet recording ink) has been used. Solvent system recording ink has a problem by the environmental safety aspect, in order to use a solvent, and the application is limited to use in office, a home, etc. by the not suitable reason. In the most common aqueous recording ink used for the object for office, or an ink jet printer for home use, since water-soluble coloring matter (color) is used, there is a problem that the water resisting property of a printing object and lightfastness are inadequate. And such a thing is the same not only about ink jet recording ink but the recording ink for writing implements.

[0003] In order to solve the above-mentioned problem, the recording ink which distributed pigments, such as carbon black which is excellent in a water resisting property and lightfastness as a color material, is partly used into the aqueous medium, but especially, conventional recording ink is inadequate in respect of the scuff resistance of a printing object, and when a printing object is ground against a fluorescence marker etc., it has problems, such as producing dirt.

[0004] Although the recording ink which added various macromolecules as a binder is examined in order to solve the above-mentioned problem, regurgitation stability is spoiled by the reasons of a rise of viscosity etc. and the recording ink with which are satisfied of all the regurgitation stability of recording ink, the printing concentration of a printing object, the scuff resistance, and marker-proof nature is not yet obtained as a result. Especially when aiming at a notice of a printing object etc., the record approach recorded on support surfaces, such as paper and a resin film, with an ink jet method to the exclusive record sheet possessing an ink absorbing layer is being adopted. In this case, when it is going to acquire good dischargeability and preservation stability, there is a problem which becomes inadequate [ the so-called glossy paper with a smooth front face / the scuff resistance of a printing object or gloss ], and becomes inadequate [ the so-called high mat paper of surface roughness / the printing concentration of a printing object ].

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[Translation done.]



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**EFFECT OF THE INVENTION**

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[Effect of the Invention] Also when according to this invention explained above it excels in preservation stability or dischargeability and records on a regular paper especially as the object for ink jet record, or an object for writing implements, the recording ink which is excellent in the printing concentration of a record object, scuff resistance, a water resisting property, lightfastness, etc. is offered.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] It is in offering the recording ink which this invention is made in view of the above-mentioned actual condition, and the purpose is excellent in preservation stability or dischargeability, and is especially excellent in the printing concentration of a printing object, scuff resistance, marker-proof nature, a water resisting property, lightfastness, etc. also when it records on exclusive glossy paper, exclusive mat paper, a regular paper, etc. as the object for ink jet record, or an object for writing implements. Moreover, other purposes of this invention are to offer the ink jet record approach which used the above-mentioned recording ink.

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**MEANS**

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[Means for Solving the Problem] As a result of examining many things, by making pigment-content powder recording ink contain a specific macromolecule, and making the range of the surface tension of the recording ink concerned optimize, this invention persons acquired knowledge that the above-mentioned purpose can be attained easily, and resulted in completion of this invention.

[0007] That is, the 1st summary of this invention has one or more association chosen from a pigment (a) and the group which changes from amide association, a urethane bond, and urea association to intramolecular at least, and contains the macromolecule (b) whose acid number of the free acid is 55 - 350 mgKOH/g, and consists in the recording ink characterized by surface tension being 25 - 54 dyne/cm. And the 2nd summary of this invention consists in the ink jet record approach characterized by what is recorded on the sheet for record which an ink absorbing layer is established at least in one side of a base material, and changes using the above-mentioned recording ink.

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. First, the pigment (a) used by this invention is explained. In this invention, you may be any of an organic pigment and an inorganic pigment, and these examples are as follows.

[0009] As a pigment used for yellow ink, the C.I. pigment yellow 1, 2, 3, 12, 13, 14, 16, 17, 73, 74, 75, 83, 93, 95, 97, 98, 114, 128, 129, and 151 and 154 grades are mentioned. As an example of the pigment used for Magenta ink, the C.I. pigment red 5, 7, and 12, 48(calcium) C.I.48(Mn), 57 (calcium), 57:1, 112, 123, 168 and 184, and 202 grades are mentioned. As an example of the pigment used for cyanogen ink, the C.I. pigment blues 1, 2, 3, 15:3, 15:34, 16, 22, 60, and 4 and 60 grades are mentioned.

[0010] The C.I. pigment [ besides above ] red 209, 122, 224, 177, and 194, C.I. pigment Orange 43, the C.I. bat violet 3, the C.I. pigment violet 19, 23, and 37, C.I. pigment Green 36 and 7, the C.I. pigment blue 15:6, and 209 grades can also be used.

[0011] moreover, this invention — if it is, various kinds of carbon black, such as acetylene black, channel black, and furnace black, can be used as a pigment. In these, channel black or furnace black is desirable, and especially furnace black is desirable.

[0012] although the DBP oil absorption of the above-mentioned carbon black is usually 60ml / 100g or more from the viewpoint of printing concentration — desirable — 100ml/— 100g or more is 140ml / 100g or more still more preferably. Volatile matter is usually 4 or less % of the weight preferably 8 or less % of the weight. although pH is usually set to 1-14 — from a viewpoint of the preservation stability of recording ink — desirable — 3-11 — it is 6-9 still more preferably. although a BET specific surface area is usually carried out to more than 100m<sup>2</sup>/g — desirable — 150-600m<sup>2</sup>/g — < — it is 260-500m<sup>2</sup>/g still more preferably. Although primary particle diameter is usually set to 30nm or less, it is 15nm or less especially preferably 16nm or less still more preferably 20nm or less preferably. Here, DBP oil absorption is JIS. K6221 The value and volatile matter which were measured by A law are JIS. The value and primary particle diameter which were measured by the approach of K6221 are an arithmetic mean diameter (number average) by the electron microscope.

[0013] As an example of the above carbon black, "Color BlackFW1", "FW2", "FW2V", "FW18", "FW200", "SpecialBlack 6", "Color Black S170" (above Degussa product),

"CONDUCTEX975ULTRA" (colon BIAN product), etc. are mentioned.

[0014] Moreover, in this invention, the things (graft-ized processing, thing made to adsorb beforehand before distributing a dispersant) which combined physically or chemically the things (oxidation treatment, fluorination processing, etc.) and dispersant which processed the above-mentioned pigment chemically, the surfactant, etc. can be used. As an example of such a thing, Cab-o-jet 200 or Cab-o-jet300 (above the Cabot Corp. make, a trade name) is mentioned. In this invention, carbon black is suitably used especially in the pigment mentioned above.

[0015] Next, it has one or more association chosen from the group which is used by this invention, and which changes from amide association, a urethane bond, and urea association to intramolecular, and the macromolecule (b) whose acid number of a free acid is 55 - 350 mgKOH/g is explained.

[0016] The giant molecule compounded so that it might have amide association in intramolecular, it might have amide association in a principal chain besides the giant molecule obtained by carrying out the polymerization of the unit which has amide association of acrylamide (meta), vinyl pyrrolidone, etc., for example as a giant molecule whose acid number of a free acid is 55 - 350 mgKOH/g, and the unit which has acid radicals, such as an acrylic acid (meta), and it might have an acid radical in a side chain is mentioned. As for these macromolecules, it is desirable to use it as a copolymer with other configuration units in respect of scuff resistance and marker-proof nature. The macromolecule which has a hydrophobic radical especially is desirable. In addition, the above-mentioned acrylamide (meta) points out the thing of methacrylamide and/or acrylamide, and an acrylic acid (meta) points out a methacrylic acid and/or an acrylic acid.

[0017] The organic radical which has rings, such as a phenyl group which may be permuted, benzyl, and a naphthyl group, as the above-mentioned hydrophobic radical, the alkyl group which are four or more carbon numbers, and may be branched or permuted, an alkenyl radical, an alkynyl group, a cycloalkyl radical, etc. are mentioned. Especially, the organic radical on which a carbon number has the organic radical and/or ring of 4-10 is desirable. As an example of a monomer of having a hydrophobic group, styrene, benzyl (meta) acrylate, ethylhexyl (meta) acrylate, hexyl (meta) acrylate, butyl (meta) acrylate, etc. are mentioned.

[0018] Moreover, as an example of a giant molecule (b) in which the acid number of a free acid is 100 - 350 mgKOH/g, acrylamide / ethylhexyl methacrylate / methacrylic-acid copolymer, dimethyl acrylamide / benzyl methacrylate / methacrylic-acid copolymer, diacetone acrylamide / methyl methacrylate / butyl acrylate / methacrylic-acid copolymer, methacrylamide / styrene / acrylic-acid copolymer, etc. are mentioned especially.

[0019] As an example of a monomer of having amide association, although an acrylamide derivative, methacrylamide derivatives, etc., such as diethyl acrylamide, propyl acrylamide, diisopropyl methacrylamide, and diacetone acrylamide, can be used in addition to acrylamide, methacrylamide, and dimethyl acrylamide, acrylamide, methacrylamide, dimethyl acrylamide, dimethyl methacrylamide, monomethyl acrylamide, and monomethyl methacrylamide are desirable in respect of preservation stability and regurgitation stability.

[0020] the rate of a monomer of having amide association in a macromolecule — from a viewpoint of scuff resistance and dischargeability — usually — more than 10mol% — it is 10-50-mol% preferably. the rate of the hydrophobic monomer in a macromolecule — from a viewpoint of marker-proof nature — usually — more than 10mol% — desirable — more than 20mol% — it is 20-mol% - 70-mol% still more preferably. the monomer which has amide association in a macromolecule — comparatively (mol%) — the ratio (mol%) of the rate of a hydrophobic monomer — from a viewpoint of preservation stability and dischargeability — usually — it is 1/3 or more still more preferably 1/5 or more preferably 1/15 or more.

[0021] Have a urethane bond in intramolecular and as a macromolecule whose acid number of a free acid is 55 - 350 mgKOH/g Mainly For example, a diisocyanate compound and diol compounds, such as polyether diols, polyester diols, and polycarbonate diols, various kinds of urethane system resin (aliphatic series system urethane resin —) water-soluble [ which is reacted and acquired in acid radical content diols, such as a carboxylic-acid radical and a sulfonic group, ], or water-dispersion Aromatic series system urethane resin, ester system urethane resin, ether system urethane resin, carbonate system urethane resin, etc. are mentioned.

[0022] As the above-mentioned diisocyanate, for example Hexamethylene di-isocyanate, Aliphatic

series diisocyanate compounds, such as hexamethylene di-isocyanate, 2 and 2, and 4-trimethyl hexamethylene di-isocyanate, Isophorone diisocyanate, hydrogenation xylylene diisocyanate, 1, 4-cyclohexane diisocyanate, Cycloaliphatic diisocyanate compounds, such as 4 and 4'-dicyclohexylmethane diisocyanate, Aromatic aliphatic series diisocyanate compounds, such as xylylene diisocyanate and tetramethyl xylenediisocyanate, Aromatic series diisocyanate compounds, such as toluylene di-isocyanate and phenylmethane diisocyanate, the denaturation objects (a carbodiimide, urethodione, URETO imine content conversion object, etc.) of these diisocyanate, etc. are mentioned.

[0023] With the above-mentioned diol compound, poly lactone diols, such as polyester diols, such as polyether diols, such as a polyethylene glycol, a polypropylene glycol, a polytetramethylene ether glycol, and polyhexamethylene ether glycol, a polyethylene horse mackerel peat, a polybutylene horse mackerel peat, a poly neopentyl horse mackerel peat, a Polly 3-methyl pentyl horse mackerel peat, polyethylene / butylene horse mackerel peat, and poly neopentyl / hexyl horse mackerel peat, and the poly caprolactone diol, and polycarbonate diol are mentioned. The diol compound of a polyether system or a polyester system is especially desirable.

[0024] As the above-mentioned acid radical content diol, a dimethylol acetic acid, dimethylol propionic acid, dimethylol butanoic acid, etc. are mentioned, for example. Especially dimethylol propionic acid is desirable.

[0025] Urethane system resin may be compounded by the prepolymer method, and may use the polyhydroxy compound of low molecular weight in that case. As a polyhydroxy compound of low molecular weight, trihydric alcohol, such as a glycol mentioned as a raw material of the above-mentioned polyester diol and an alkylene oxide low mol addition product, a glycerol, trimethylolethane, and trimethylol propane, the alkylene oxide low mol addition product of those, etc. are mentioned.

[0026] moreover — while neutralizing an urethane prepolymer after it neutralizes the acid radical originating in a dimethylol alkane acid or — water extension — or JI or triamine extension can be carried out. As polyamine used in the case of amine extension, diamine or triamine is usually mentioned. Moreover, a hexamethylenediamine, isophorone diamine, a hydrazine, a piperazine, etc. are mentioned as the example. As a base used in the case of the above-mentioned neutralization, inorganic bases, such as alkanolamines, such as alkylamines, such as a butylamine and triethylamine, monoethanolamine, diethanolamine, and triethanolamine, a morpholine, ammonia, and a sodium hydroxide, are mentioned, for example.

[0027] It has urea association in intramolecular, and the giant molecule whose acid number of a free acid is 55 – 350 mgKOH/g can be obtained by the above-mentioned water extension, JI, or triamine extension as a giant molecule which has a urethane bond and urea association. Moreover, in the case of the giant molecule which has only urea association in intramolecular, it can obtain by the reaction of diisocyanate and acid radical content diamine.

[0028] In this invention, as a macromolecule (b), urethane system resin is desirable and the urethane resin of an ester system, an ether system, or an aromatic series system is desirable especially. Each above-mentioned giant molecule (b) can be used in forms, such as organic amine salts, such as alkali-metal salts, such as Li, Na, and K, ammonia, dimethylamine, and ethanolamine (monochrome, JI, Tori).

[0029] Although the acid number of the free acid of the above-mentioned macromolecule (b) used by this invention is 55 – 350 mgKOH/g as above-mentioned, from a viewpoint which raises further the preservation stability and regurgitation stability of recording ink, the minimums of the acid number are 65 mgKOH/g still more preferably 60 mgKOH/g preferably, and the upper limits of the acid number are 300 mgKOH/g still more preferably 330 mgKOH/g preferably. Moreover, the acid number of the free acid of the macromolecule (b) which can be used for the application (for example, for desktops) for which a regular paper (and chiefly form) is used is 100 – 350 mgKOH/g preferably. Furthermore, the minimums of the acid number in this case are 150 mgKOH/g still more preferably 120 mgKOH/g preferably, and the upper limits of the acid number are 300 mgKOH/g still more preferably 330 mgKOH/g preferably. The acid number of the free acid of the macromolecule (b) which can be used for the application (for example, for a large format) for which only a form is used chiefly on the other hand is 55 – 150 mgKOH/g preferably. Furthermore, the minimums of the acid number in this case are 65 mgKOH/g still more preferably 60 mgKOH/g preferably, and the upper limits of the acid

number are 100 mgKOH/g still more preferably 130 mgKOH/g preferably. moreover, the weight average molecular weight of the above-mentioned macromolecule (b) — from a viewpoint of regurgitation stability — usually — 300,000 or less — desirable — 5000–45,000 — further — desirable — 5000–30,000 — it is 5000–20,000 especially preferably.

[0030] Various additives can be used for the recording ink concerning this invention, for example, various kinds of anionic detergents, the Nonion nature surfactant, a cationic surfactant, an amphoteric surface active agent, a water soluble polymer, etc. are mentioned.

[0031] As an anionic detergent, fatty-acid salts, alkyl-sulfuric-acid ester salts, Alkylbenzene sulfonates and alkyl naphthalenesulfonate Alkyl sulfo succinate and alkyl diphenyl ether disulfon acid chloride Alkyl phosphate, polyoxyethylene alkyl-sulfuric-acid ester salts, Polyoxyethylene alkyl aryl sulfate salts and alkane sulfonates naphthalene sulfonic-acid formalin condensates, polyoxyethylene alkyl phosphoric ester, and N-methyl-N-me — oil taurine acid chloride and alpha olefin sulfonates are mentioned.

[0032] Especially as a nonionic surfactant, although not restricted, what has ethyleneoxide structure or propylene oxide structure from the point of preservation stability and printing concentration is desirable, and the thing of 9–17, especially 10–16 has still more desirable HLB also in it.

[0033] As an example of a nonionic surfactant, the polyoxyethylene nonylphenyl ether, Polyoxyethylene octyl phenyl ether, polyoxyethylene alkyl ether, The polyoxyethylene lauryl ether, the polyoxyethylene oleyl ether, The polyoxyethylene tridecyl ether, the polyoxyethylene cetyl ether, Polyoxyethylene stearylether, polyoxyethylene alkylamine, An amino polyoxyethylene, a sorbitan fatty acid ester, polyoxyethylenesorbitanlaurate, Polyoxyethylene sorbitan palmitate, polyoxyethylene sorbitan stearate, Polyoxyethylene sorbitan oleate, a naphthol ethylene oxide addition product, An acetylene glycol ethylene oxide addition product, a bisphenol A ethylene oxide addition product, Oxyethylene oxypropylene block polymer, a sorbitan fatty acid ester, Polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, etc. are mentioned.

[0034] On the other hand, as a cationic surfactant and an amphoteric surface active agent, alkylamine salts, quarternary ammonium salt, alkyl betaines, and amino KISAIDO are mentioned.

[0035] In addition, the other various water soluble polymers may be used together with the aforementioned macromolecule (b).

[0036] As an anionic water soluble polymer, 200 or more mgKOH/g of acid numbers in the form of the viewpoint of preservation stability of recording ink to a free acid is 150 or more mgKOH/g usually still more preferably suitable for the thing of 250 or more mgKOH/g preferably. Furthermore, the copolymer which has a hydrophobic radical is desirable in respect of the distributed stability of carbon black, the water resisting property of a printing object, and scuff resistance.

[0037] Although the organic radical which has rings, such as a phenyl group which may be permuted, benzyl, and a naphthyl group, as a hydrophobic radical in a giant molecule, the alkyl group which are four or more carbon numbers, and may be branched or permuted, an alkenyl radical, an alkynyl group, a cycloalkyl radical, etc. are mentioned, the organic radical which has a ring especially is desirable.

[0038] As an anionic water soluble polymer used by this invention Specifically Styrene (alpha-methyl) / maleic-acid copolymer, styrene (alpha-methyl) / (meta) acrylic-acid copolymer, That it is \*\*\*\* in styrene / (meta) acrylic ester / (meta) acrylic-acid copolymer, acrylic ester (meta) / (meta) acrylic-acid copolymer, acrylic ester (meta) / maleic-acid copolymer, and/or these (alpha-methyl) \*\*\*\*\* They are styrene (alpha-methyl) / (meta) acrylic-acid copolymer preferably. Here, styrene (alpha-methyl) points out the thing of alpha methyl styrene and/or styrene, and an acrylic acid (meta) points out the thing of a methacrylic acid and/or an acrylic acid.

[0039] Moreover, although any of block polymer, a graft polymer, and a random polymer are sufficient as the anionic water soluble polymer used by this invention, a point to its graft polymer or random polymer of a manufacturing cost is desirable, and especially its random polymer is mainly desirable. Moreover, as for weight average molecular weight, 50,000 or less are desirable, 15,000 or less are still more desirable, and 10,000 especially or less are more desirable than the viewpoint of regurgitation stability. Furthermore, the acid number can use the copolymer of 150 or more mgKOH/g in forms, such as organic amine salts, such as alkali-metal salts, such as Li, Na, and K, ammonia, dimethylamine, and ethanolamine (monochrome, JI, Tori).

[0040] As a commercial item of the above giant molecules or a polymer solution, the "JON krill 67" by the Johnson polymer company, "678", "680", "682", "690" and/or its salt, the "JON krill 52", "57", "60", "62", "63", "70", "354", "501", "6610", etc. are mentioned.

[0041] Although the aqueous medium which makes water a subject is usually used as a medium of the recording ink of this invention, it is desirable to add and use a water-soluble organic solvent for water in this case.

[0042] As the water-soluble above-mentioned organic solvent, ethylene glycol, propylene glycol, 1, 3-propanediol, a butylene glycol, a diethylene glycol, triethylene glycol and a polyethylene glycol (example: — "#200" by Wako Pure Chem —) "#300", "#400", "#4000", "#6000", A glycerol, N-methyl pyrrolidone, 1, 3-dimethyl imidazolinone, Thiodiglycol, 2-pyrrolidone, a sulfolane, dimethyl sulfoxide, Diethanolamine, triethanolamine, methanol, ethanol, isopropanol, neopentyl alcohol, trimethylol propane, 2, and 2-dimethyl propanol etc. is mentioned.

[0043] In this invention, since the surface tension of recording ink is lowered and the osmosis rate to the space of ink and the rate of drying of a record object are raised, the Nonion nature surfactant of low molecular weight can be used.

[0044] As an example of the Nonion nature surfactant of the above-mentioned low molecular weight Ethylene glycol monomethyl ether, ethylene glycol wood ether, Ethylene glycol monoethyl ether, ethylene glycol diethylether, The ethylene glycol mono—n-propyl ether, ethylene glycol mono—isopropyl ether, Ethylene glycol mono—n-butyl ether, ethylene glycol mono—sec-butyl ether, The ethylene glycol mono—isobutyl ether, ethylene glycol mono—tert-butyl ether, Ethylene glycol mono—n-amyl ether, the ethylene glycol mono—n-hexyl ether, Propylene glycol monomethyl ether, propylene glycol wood ether, The propylene glycol monoethyl ether, propylene glycol diethylether, The propylene glycol mono—n-propyl ether, propylene glycol mono—isopropyl ether, Propylene glycol mono—n-butyl ether, propylene glycol mono—sec-butyl ether, The propylene glycol mono—isobutyl ether, propylene glycol mono—tert-butyl ether, The diethylene-glycol monomethyl ether, diethylene-glycol wood ether, Diethylene glycol monoethyl ether, the diethylene-glycol mono—n-propyl ether, Diethylene-glycol mono—isopropyl ether, diethylene-glycol mono—n-butyl ether, Diethylene-glycol mono—sec-butyl ether, the diethylene-glycol mono—isobutyl ether, Diethylene-glycol mono—tert-butyl ether, dipropylene glycol monomethyl ether, The dipropylene glycol monoethyl ether, the dipropylene glycol mono—n-propyl ether, Dipropylene glycol mono—n-butyl ether, the polyethylene-glycol monopropyl ether, The polyethylene-glycol monobutyl ether, the ethylene glycol addition product of a glycerol (example: RIPONIKKU EG-1 (product made from RIPOKEMIKARU) etc.), The ethylene glycol addition product of acetylene glycols (example: SAFI Norian 440, SAFI Norian 465, SAFI Norian 485 (Nissin Chemical Industry make), ASECHIRE Norian EH, ASECHIRE Norian EL (above, Kawaken Fine Chemicals make), etc. are mentioned.)

[0045] the amount of the Nonion nature surfactant used of low molecular weight — the recording ink 100 weight section — receiving — usually — 0.5 – 50 weight section — desirable — 2 – 30 weight section — it is 5 – 20 weight section still more preferably. Although the surface tension of recording ink is appropriately controlled by the class and the amount of the Nonion system surfactant of the low molecular weight used, it is necessary to make surface tension of the recording ink of this invention into the range of 25 – 54 dyne/cm. As a result of osmosis of the recording ink to a recorded material becoming slow when it prints as recording ink if surface tension becomes larger than 54 dyne/cm, the fault that printing speed must be made late occurs. Moreover, in the range where the surface tension of recording ink is smaller than 25 dyne/cm, since osmosis of the recording ink to a recorded material becomes large too much, printing concentration is spoiled.

[0046] And by 25 or more dyne/cm less than 37 dyne/cm, urethane system resin is suitably used for the surface tension of recording ink as a macromolecule (b) the preservation stability of recording ink, and in respect of scuff resistance among the above-mentioned range. Moreover, when the surface tension of recording ink is 37 or more dyne/cm less than 54 dyne/cm, the polymer which makes an acrylamide derivative and/or a methacrylamide derivative a part of configuration unit is suitably used as a macromolecule (b).

[0047] When it sees from the class of print sheet, in the case of an application (for example, for desktops) which is used for the above-mentioned regular paper (and chiefly form), in respect of the printing concentration of recording ink mainly moreover, the surface tension of recording ink

Preferably 37 or more dyne/cm Usually, 40 or more dyne/cm, It is the range of 40 – 50 dyne/cm preferably. Furthermore, moreover, in the case of the above-mentioned application (for example, for a large format) which is chiefly used only for a form 35 or less dyne/cm of surface tension of recording ink is less than 37 dynes [/cm ] usually the range of 30 – 35 dyne/cm still more preferably preferably in respect of printing concentration and printing speed.

[0048] Other additives, such as antiseptics besides the above, an antifungal agent, a germicide, pH regulator, and a urea, may be used for the recording ink of this invention if needed.

[0049] According to a well-known approach, the recording ink of this invention carries out distributed processing of the pigment (a) in a medium to the bottom of existence of the aforementioned macromolecule (b) and the required aforementioned addition component, and obtains high-concentration dispersion liquid. Subsequently It is obtained by the approach of carrying out distributed processing of the pigment (a) to the bottom of existence of a macromolecule (b) and the required aforementioned addition component in the method (the masterbatch method) of adding a medium to the obtained dispersion liquid, performing concentration adjustment, and preparing recording ink, or a medium, and preparing recording ink. Since distributed processing is performed by high concentration, the above-mentioned masterbatch method is efficient.

[0050] Jet mills which can carry out grinding processing as a disperser as a disperser used for distributed processing, without using media besides a ball mill, a roll mill, and SANDOGURAINDOMIRU, such as a nano mizer and Altima IZA, are used. A jet mill with little contamination which originates in SANDOGURAINDOMIRU or media especially is desirable. In this invention, a filter or a centrifugal separator removes a big and rough particle after grinding and distributed processing by the above-mentioned disperser.

[0051] The amount of the pigment (a) used is 1 – 10 % of the weight usually 2 – 6 % of the weight still more preferably two to 8% of the weight preferably to all recording ink weight. It has one or more association chosen from the group which changes from amide association, a urethane bond, and urea association to intramolecular, and the amount of the macromolecule (b) used whose acid number is 55 – 350 mgKOH/g is 5 – 200 % of the weight usually 8 – 70 % of the weight still more preferably eight to 100% of the weight preferably to the weight of a pigment (a). Moreover, the amount of the water-soluble above-mentioned organic solvent used is comparatively carried out in recording ink from a viewpoint of the preservation stability of recording ink, and is 5 – 30 % of the weight usually 8 – 20% of the weight of the range still more preferably five to 20% of the weight preferably.

[0052] The range of 0.05–0.2 micrometers of mean particle diameter of the pigment in recording ink is 0.01–0.3 micrometers usually from a viewpoint of distributed stability, regurgitation stability, and record concentration 0.1–0.2 micrometers still more preferably preferably. As for the maximum grain size of a pigment, it is desirable from a viewpoint of distributed stability and regurgitation stability that it is 5 micrometers or less. Moreover, 5–60nm of standard deviation in the distributed particle size distribution of the pigment in recording ink is 70nm or less usually preferably set to 10–50nm still more preferably from a viewpoint of the preservation stability of recording ink, regurgitation stability, and record concentration.

[0053] However, let an above-mentioned mean-dispersion particle size and distributed particle size distribution be the value measured with the particle-size-distribution meter:Nikkiso [ Co., Ltd. ] Co., Ltd. product "the micro truck UPA150."

[0054] The recording ink of this invention cannot stop at the object for ink jets, and writing implements, but can also be used as recording ink of other applications. Especially the recording ink of this invention is suitable for ink jet record. And although chiefly divided roughly into a form, the recording ink of the multilayer structure which the ink absorbing layer is established in at least the regular paper of 1 layer structure to which a recorded material changes from a cellulose, a loading material, a sizing compound, etc., and one side of a base material, and changes which is this invention can be used for all recorded materials (a regular paper, recycled paper, the papers only for ink jets (coat paper, glossy paper, etc.), the films only for ink jets (a coated film, gloss film, etc.), OHP film, etc.).

[0055] Next, the ink jet record approach concerning this invention is explained. In this invention, all the types of an on demand method, continuous method, and piezo method, a thermal method, etc. of the ink jet record approach is employable.



[0056] In this invention, the sheet for record which an ink absorbing layer is established at least in one side of a base material, and changes is used.

[0057] As a base material, addition components, such as a binder, a sizing compound, a fixing agent, a yield improver, a cation-ized agent, and a paper reinforcing agent, are mixed in the principal component which consists of wood pulp and pigments, such as chemical pulp, mechanical pulp, and recycled pulp, and the stencil paper manufactured with various equipments, such as a Fortlinear paper machine, a cylinder machine, and a twin-wired paper machine, is used for it. Moreover, what prepared resin layers, such as polyolefine besides the art paper and coat paper which prepared the coat layer on stencil paper, and cast coated paper, can be used. Furthermore, you may be the film (or sheet) which consists of synthetic resin and such mixture, such as polyethylene, polypropylene, polyester, nylon, rayon, polyurethane, and polyethylene terephthalate. These base materials are suitably chosen in consideration of the application of the record purpose and a record image, adhesion with an ink absorbing layer, etc.

[0058] An ink absorbing layer is formed by applying the binder resin with which the non-subtlety particle (white pigments) was distributed on the surface of the base material.

[0059] As a non-subtlety particle, precipitated calcium carbonate, whiting, a kaolin, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc sulfide, zinc carbonate, a satin white, aluminum silicate, diatomaceous earth, a calcium silicate, synthetic amorphous silica, an aluminum hydroxide, a lithopone, a zeolite, hydrated halloysite, a magnesium hydroxide, alumina sol, fumed silica, colloidal silica, etc. are mentioned, for example. Moreover, the colloidal silica covered with the cation modifier which consists of metal oxidization hydrates, such as an aluminum oxide hydrate, a zirconium dioxide hydrate, and a tin-oxide hydrate, can also be used. These non-subtlety particles may use two or more sorts together. In addition, since the mean particle diameter of a non-subtlety particle changes with glossy paper and mat papers, it is chosen from the suitable range, respectively.

[0060] As binder resin, for example, polyvinyl alcohol, vinyl acetate, Cellulosics, such as oxidization starch, etherification starch, a carboxymethyl cellulose, and hydroxyethyl cellulose, Conjugated diene system polymerization latexes, such as maleic-anhydride resin, a styrene-butadiene copolymer, and a methyl methacrylate-butadiene copolymer Acrylic polymerization latexes, such as a polymer (\*\*) of acrylic ester, (Meta) The functional-group denaturation polymerization latexes by functional-group content monomers, such as a carboxyl group of vinyl system polymerization latexes, such as an ethylene-vinyl acetate copolymer, and these various polymers Polymethylmethacrylate, polyurethane resin, a vinyl chloride vinyl acetate copolymer, Thermosetting synthetic resin, such as an unsaturated polyester resin besides a polyvinyl butyral, casein, gelatin, soybean protein, and silyl denaturation polyvinyl alcohol, an alkyd resin, melamine resin, and a urea-resin, is mentioned.

[0061] Moreover, in this invention, a cationic organic substance can be used together in order to raise fixable [ of the carbon black as a color material ]. As this cationic organic substance, amines, such as quarternary ammonium salt and alkylamine, and amides are mentioned, for example. Moreover, the giant molecule which has such cationic residue in a side chain can also be used as a cationic organic substance.

[0062] Furthermore, as other additives, a pigment agent, a thickener, a fluid amelioration agent, a defoaming agent, foam suppressor, a release agent, a foaming agent, a penetrating agent, a coloring color, a color pigment, a fluorescent brightener, an anti-oxidant, antiseptics, an antifungal agent, a deck-watertight-luminaire-ized agent, a humid paper reinforcing agent, etc. can be blended suitably.

[0063] formation of an ink absorbing layer is [ size press / various blade coaters, a roll coater, an air knife coater, bar coater, rod blade coater, curtain coater, short dwell coater, ] well-known — it is carried out by carrying out various equipment use.

[0064] As for an ink absorbing layer, it is desirable to form the porous layer. 1 micrometers or more of average pore size of a porous layer are 0.5 micrometers or more usually from the printing concentration of a printing object, and a viewpoint of scratch-proof nature 2 micrometers still more preferably preferably. Here, the scanning electron microscope photograph on the front face of a record sheet is taken for two or more scale factors, and after digitizing by the scanner inputting method, the arithmetic mean diameter (number average) which computed and searched for distribution of the diameter of circle (grade area circle diameter) which has an area equal to the area of each opening part extracted by computer image analysis is called average pore size.

[0065] The above-mentioned recording ink concerning this invention is [ as opposed to / especially / the sheet for record possessing the ink absorbing layer of the comparatively high mat tone of surface roughness ] useful. therefore, S.A.D. on the above-mentioned front face of an ink absorbing layer (Surface Area Difference) — usually — still more preferably is preferably taken or more for 70 60 or more 50 or more. In this case, the printing object which was extremely excellent in printing concentration and scratch-proof nature can be obtained.

[0066] Above-mentioned S.A.D. is one of the indexes showing surface roughness, and a surface specific surface area is specifically expressed and it defines as the following formula (I). In this invention, S.A.D. is measured and computed on the conditions shown in the following table 1. However, in the area at the time of the area of all the triangles formed by three data points with which Si adjoined, and Pi projecting Si on XY flat surface, and sigmaSi, all the sums of si and sigmaPi (s) express all the sums of Pi among a formula (I).

[0067]

[Equation 1]  $S.A.D. = \{(\sigma Si / \sigma Pi) - 1\} \times 100 (\%)$

[0068]

[Table 1] (Measuring method)

equipment: — Scanning Probe Microscope model: — Digital Instruments Shrine make NanoScope III Scanner: J-Head measurement field: — 1 micrometer x 1-micrometer pixel number: — 512 x 512 Scan Rate: 1.0 Hz measurement mode: — Tapping AFM probe: — digital INSU vine face company make NCH-W

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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EXAMPLE

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples, unless the summary is exceeded. They are weight criteria unless especially the "section" and "%" have a notice in many following examples. Moreover, measurement and the evaluation approach of physical properties are as follows at the used carbon black list.

[0070]

[Table 2]

<カーボンブラック>

	窒素吸着比表面積 ( $\text{m}^2/\text{g}$ )	DBP吸油量 ( $\text{ml}/100\text{g}$ )	1次粒子径 ( $\text{nm}$ )
カーボンブラック (A)	290	150	14
カーボンブラック (B)	350	86	12

[0071] (1) Printing trial : the ink jet printer was filled up with recording ink, solid printing was carried out at the paper only for ink jet printers (mat paper, glossy paper), and/or a regular paper (copy paper), and the criteria of the following three-stage estimated.

[0072]

[Table 3] O : there is no printing omission and the printing object also with the good grace of the edge section was obtained.

\*\* : Although there is a printing omission faintly, it is satisfactory practically.

x : A printing omission is remarkable.

[0073] (2) Printing concentration evaluation : the concentration of the printing object obtained by the above-mentioned printing trial was measured using the Macbeth concentration meter (RD914). It was shown that printing concentration is so good that a numeric value is large, and when it was 1.5 or more, it judged with success.

[0074] (3) Scuff resistance trial : it set in the printing object obtained by the above-mentioned printing trial, after recording ink was dried and established, the printing solid section was lightly ground against the metal spoon, and the criteria of the following three-stage estimated the scuff resistance of recording ink.

[0075]

[Table 4]

O : there is no peeling of recording ink and a recorded material front face is not exposed.

\*\* : Although there is peeling of recording ink faintly, it is satisfactory practically.

x : Peeling of recording ink is remarkable.

[0076] (4) Marker-proof trial : in the printing object obtained by the above-mentioned printing trial, the alphabetic character section was traced with the commercial yellow fluorescence marker (ZEBRA product OPTEX) 24 hours after after a printing trial, and the criteria of the following three-stage estimated the marker-proof nature of ink.

[0077]

[Table 5] O : there is almost no dirt of the alphabetic character section ground with the marker.

\*\*: Although there is dirt of the alphabetic character section ground with the marker faintly, it is satisfactory practically.

x: The dirt of the alphabetic character section ground with the marker is remarkable.

[0078] (5) Distributed particle-size-distribution measurement : recording ink was diluted with ion exchange water, and distributed particle size distribution was measured with the particle-size-distribution plan (Nikkiso [ Co., Ltd. ] Co., Ltd. product "the micro truck UPA150").

[0079] (6) Measurement of the average pore size of an ink absorbing layer, and the mean particle diameter of white pigments : first, the scanning electron microscope (SEM) photograph on the front face of a record sheet (one 150 times the scale factor after enlargement of this) was inputted by 360dpi from the scanner, computer image processing was performed and digital imaging was carried out. The value of 1 pixel corresponded to 0.465 micrometers. The 512x512-pixel image of six sheets was processed similarly, and a total of 1723 pores (opening section) were extracted. It asked for the diameter of circle (grade area circle diameter) which has area [ area / of each extracted pore ], and average pore size (number average value) was computed from the distribution. The measurement result about the paper only for ink jet records of marketing with which the printing trial was presented is shown in Table 9.

[0080] (7) Measurement of S.A.D. on the front face of an ink absorbing layer : it measured by the approach given in the text about five on the front face of an ink absorbing layer (five fields), and the average was adopted. The measurement result about the paper only for ink jet records of marketing with which the printing trial was presented is shown in Table 9.

[0081] (8) Surface tension measurement : record liquid junction side tension was measured using the UIRUHERUMI mold surface tension measurement machine "CBVP-Z" (consonance interface science company make).

[0082] The ethanol 200 section was put into the four-lot flask furnished with synthetic example 1 reflux condenser of a high molecular compound, a thermometer, the glass tube for nitrogen purges, and stirring equipment, the azobisisobutironitoriru(azobisisobutyronitril) 2 section was added, and reflux heating was carried out at 80 degrees C under the nitrogen air current. The mixture of the dimethyl acrylamide 25 section, the benzyl methacrylate 44 section, the methacrylic-acid 31 section, and the lauryl mercaptan 5 section was dropped at this reaction container for 2 hours. After dropping termination, the 0.5 sections of azobisisobutironitoriru were added and the polymerization was performed for 4 hours. Subsequently, ethanol was removed and the high molecular compound was obtained.

[0083] In order to measure the acid number of the above-mentioned high molecular compound, after taking 1g of samples and dissolving in the mixed solvent of water/ethanol (50g/50g), 0.1NKOH water solutions performed the neutralization titration. Titration is JIS. Carrying out to K0113 by the potentiometric titration approach of a publication, a terminal point is JIS. K0113 It was decided by the point-of-inflection method of a publication that it would be 5.2.2. The amount of KOH needed for titration was made into the acid number. Consequently, the acid number of the above-mentioned high molecular compound was 200 mgKOH/g.

[0084] Next, under cooling, the sodium-hydroxide water solution was dropped at the flask, and it neutralized. Subsequently, ethanol was removed and the anionic macromolecule A water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 7,000 and a macromolecule is 29. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 29-mol %.

[0085] In the synthetic example 1 of the synthetic example 2 above of a giant molecule, the acid number obtained the giant molecule of 200 mgKOH/g like the synthetic example 1 except having used the mixture of the dimethyl acrylamide 15 section, the benzyl methacrylate 54 section, the methacrylic-acid 31 section, and the lauryl mercaptan 5 section. Subsequently, under cooling, after dropping the sodium-hydroxide water solution at the flask and neutralizing, ethanol was removed and the anionic macromolecule (B) water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 7,500 and a macromolecule is 18. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 38-mol %.

[0086] In the synthetic example 1 of the synthetic example 3 above of a giant molecule, the acid

number obtained the giant molecule of 200 mgKOH/g like the synthetic example 1 except having used the mixture of the dimethyl acrylamide 45 section, the benzyl methacrylate 24 section, and the methacrylic-acid 31 section. Subsequently, under cooling, after dropping the sodium-hydroxide water solution at the flask and neutralizing, ethanol was removed and the anionic macromolecule (C) water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 33,000 and a macromolecule is 48. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 14-mol %.

[0087] In the synthetic example 1 of the synthetic example 4 above of a giant molecule, the acid number obtained the giant molecule of 200 mgKOH/g like the synthetic example 1 except having used the mixture of the dimethyl acrylamide 45 section, the benzyl methacrylate 24 section, the methacrylic-acid 31 section, and the lauryl mercaptan 2 section. Subsequently, under cooling, after dropping the sodium-hydroxide water solution at the flask and neutralizing, ethanol was removed and the anionic macromolecule (D) water solution was obtained. For this macromolecule, the rate of a monomer of having amide association which weight average molecular weight occupies in 11,500 and a macromolecule is 48. The percentage of a monomer of having the hydrophobic group occupied in mol% and a macromolecule was 14-mol %.

[0088] Each component shown in Table 6 of the primary example was extracted, and the Sand grinder performed distributed processing using the zirconia beads of the diameter of an average of 0.6mm.

[0089]

[Table 6]

成 分	使用量 (部)
カーボンブラック (A)	9
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」(酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	4.5
グリセリン	5
イオン交換水	81.5
合計	100

[0090] The polyester system urethane resin solution (Takeda Chemical Industries, Ltd. make) 21.6 section obtained by the below-mentioned approach, the glycerol 22.5 section, the diethylene-glycol monobutyl ether 22.5 section, and the ion-exchange-water 58.4 section were further added to the liquid obtained above. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.139 micrometers, and the surface tension of recording ink was 33 dyne/cm. Other test results were shown in Table 10 and 11.

[0091] The above-mentioned polyester system urethane resin solution is polyester polyol 60g compounded from an adipic acid, neopentyl glycol, and 1,6-hexandiol, and 3-isocyanate methyl. - It is neutralizing by the sodium hydroxide, after making 3, 5, and 5-trimethyl cyclohexyl isocyanate [ 90 ] and 1 and 3-screw (1-isocyanate-1-methylethyl) benzene 30g, 40g [ of dimethylol propionic acid ], and triethylene glycol 5g, and 2-[(2-aminoethyl) amino] ethanol 10g react. Acid-number:70 mgKOH/g which it is obtained and is a free acid, Tg:190 degree C, Mw: They are 200,000 and solid content concentration:25%.

[0092] The polyester system urethane resin solution 9 section of the acid number 70, the glycerol 9 section, the 2-pyrrolidone 12.6 section, the isopropyl alcohol 3.6 section, and the ion-exchange-water 45.8 section were further added to the liquid obtained by carrying out distributed processing like example 2 example 1. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of

the carbon black in the obtained recording ink was 0.137 micrometers, and the surface tension of recording ink was 48 dyne/cm. Other test results were shown in Table 10 and 11.

[0093] In example of comparison 1 example 1, recording ink was prepared and evaluated like the example 1 instead of the polyester system polyurethane resin of the acid number 70 except having used the polyester system polyurethane resin of the acid number 50. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.138 micrometers, and the surface tension of recording ink was 34 dyne/cm. Although the printing test result was shown in Table 10, the scuff resistance trial was not able to be carried out because of poor printing.

[0094] In example of comparison 2 example 2, recording ink was prepared and evaluated like the example 1 instead of the polyester system polyurethane resin of the acid number 70 except having used the polyester system polyurethane resin of the acid number 50. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.140 micrometers, and the surface tension of recording ink was 33 dyne/cm. Although the printing test result was shown in Table 10, the scuff resistance trial was not able to be carried out because of poor printing.

[0095] In example 3 example 1, it evaluated by preparing recording ink like an example 1 instead of carbon black (A) except having used carbon black (B). The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.140 micrometers, and the surface tension of recording ink was 35 dyne/cm. Other test results were shown in Table 10 and 11.

[0096] Each component shown in Table 7 of the 4th example was extracted, and the Sand grinder performed distributed processing using the zirconia beads of the diameter of an average of 0.6mm.

[0097]

[Table 7]

成 分	使用量 (部)
カーボンブラック (A)	5
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」 (酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	2.5
グリセリン	3
イオン交換水	53.5
合計	64

[0098] The (Macromolecule A) water-solution 3.8 section (macromolecule 1.25 section) obtained in said synthetic example 1, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 18.2 section were further added to the liquid obtained above. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.143 micrometers, and the surface tension of recording ink was 50 dyne/cm. Other test results showed other test results in Table 12.

[0099] In example 5 example 4, recording ink was obtained like the example 4 except having used the (Macromolecule B) water-solution 3.8 section (macromolecule 1.25 section) obtained in said synthetic example 2 instead of the (Macromolecule A) water-solution 3.8 section (macromolecule 1.25 section). The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.138 micrometers, and the surface tension of recording ink was 50 dyne/cm. Other test results were shown in Table 12.

[0100] Each component shown in Table 8 of the 6th example was extracted, and the Sand grinder performed distributed processing using the zirconia beads of the diameter of an average of 0.6mm.

[0101]

[Table 8]

成 分	使用量 (部)
カーボンブラック (A)	4
スチレン-アクリル酸系共重合体 (ジョンソンポリマー社製「ジョンアクリル678」 (酸化: 215、Mw: 8500) のアンモニウム塩の20WT%水溶液)	2.0
グリセリン	3
イオン交換水	42.2
合計	51.2

[0102] The (Macromolecule B) water-solution 6.1 section (macromolecule 2.0 section) obtained in said synthetic example 2, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 28.7 section were further added to the liquid obtained above. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.139 micrometers, and the surface tension of recording ink was 48 dyne/cm. Other test results were shown in Table 12.

[0103] The (Macromolecule C) water-solution 4.1 section (macromolecule 1.0 section) obtained in said synthetic example 3, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 30.7 section were further added to the dispersion liquid obtained like example 7 example 6. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.311 micrometers, and the surface tension of recording ink was 52 dyne/cm. Other test results showed other test results in Table 12.

[0104] The (Macromolecule D) water-solution 4.7 section (macromolecule 1.6 section) obtained in said synthetic example 4, the glycerol 5 section, the isopropyl alcohol 2 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 30.1 section were further added to the dispersion liquid obtained like example 8 example 6. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.176 micrometers, and the surface tension of recording ink was 51 dyne/cm. Other test results were shown in Table 12.

[0105] The (giant-molecule B) water-solution 3.8 section (giant-molecule 1.25 section) obtained in said synthetic example 2, the glycerol 5 section, the TORIECHIREN glucoside monobutyl ether 4.0 section, the 2-pyrrolidone 7 section, and the ion-exchange-water 39 section were further added to the dispersion liquid obtained like example 9 example 6. The pressure filtration of this liquid was carried out through the filter paper of No.5C, and the liquid obtained here was used as recording ink. The mean-dispersion particle size of the carbon black in the obtained recording ink was 0.114 micrometers, and the surface tension of recording ink was 44 dyne/cm. Other test results were shown in Table 12.

[0106]

[Table 9]

	MCマット紙 (Epson 社製品)
受容層の平均細孔孔 ( $\mu\text{m}$ )	4.85
S. A. D	93.4

[0107]

[Table 10]

	印字試験	印字濃度
実施例 1	○	1. 6
実施例 2	△	—
実施例 3	○	1. 4
比較例 1	×	—
比較例 2	×	—

(試験に供した記録紙：MCマット紙)

[0108]

[Table 11]

		実施例 1	実施例 2	実施例 3
マット紙	MCマット紙 (Epson 社製品)	○	—	○
	MJ A 4 S P 1 (Epson 社製品)	○	—	○
光沢紙	H G 2 0 1 (Canon 社製品)	○	—	○
	H G 1 0 1 (Canon 社製品)	○	—	○
	MJ A 4 S P 6 (Epson 社製品)	○	—	○
	C 6 0 4 3 A (ヒューレット・パッカート 社製品)	○	—	○
普通紙	Xerox 4 0 2 4 (Xerox 社製品)	○	○	○
	Xerox 4 2 0 0 (Xerox 社製品)	○	○	○

[0109]

[Table 12]

	印字試験	印字濃度	耐マーカ性
実施例 4	○	1. 5 9	△
実施例 5	○	1. 5 5	△
実施例 6	○	1. 4 0	○
実施例 7	○	1. 5 3	△
実施例 8	○	1. 4 3	○
実施例 9	○	1. 2 8	○

(試験に供した記録紙：Xerox 4 0 2 4)

[Translation done.]



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